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# Sulfur Retention in Coal Ash

KVB, Inc, Tustin, CA

Prepared for

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Nov 78

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|---|---|---|---|---|
| Air Pollution | Loading | Air Pollution Control | 13B | |
| Coal | Oxygen | Stationary Sources | 21D | |
| Combustion Products | Linear Regression | Excess Oxygen | 21B | 12A |
| Sulfur Oxides | | Alkaline Salts | 07B | |
| Sulfur | | Sulfur Balance | | |
| Stokers | | | 13A | |
| Ashes | | | | |

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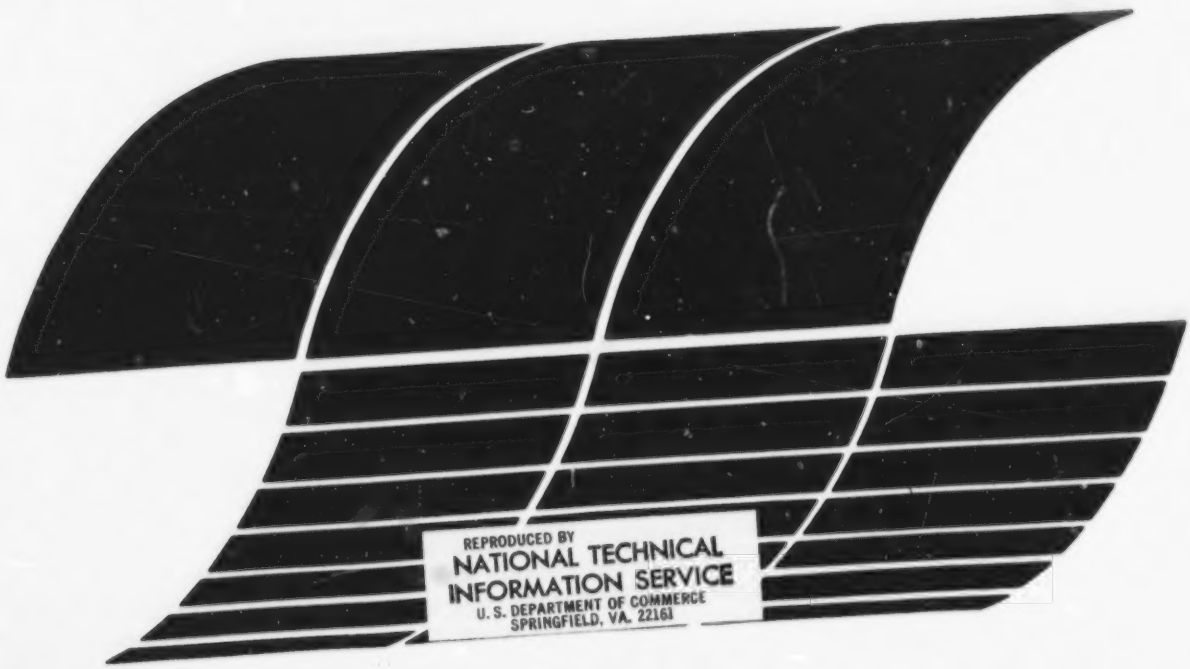

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November 1978

# Sulfur Retention in Coal Ash

by

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1 a/

## ABSTRACT

An analytical study was conducted to assess the potential for sulfur retention in various types of coal-fired boilers. The results of a field test of ten industrial coal-fired boilers were used to evaluate the impact on sulfur retention of the operating variables (load and excess $O_2$).

The effect of ash composition on sulfur retention was also evaluated with the use of a linear regression analysis. An expression of the form

$$\text{Percent Sulfur Emitted} = a+b\ (\%Na_2O/\%CaO) + C\ (\text{load}/10^5)$$

where a, b and c are constants, gave the best overall fit to the two pulverized coal-fired boiler data.

The field test results and the regression analysis results were supported by equilibrium coal ash composition calculations over a range of temperatures and theoretical air for four coal ash compositions. These calculations show that significant fractions of the sulfur can be tied up as Ca and Na salts under both reducing and oxidizing conditions at temperatures below 2500 °F. A minimum in the total condensed phase sulfur species is predicted at stoichiometric conditions for all temperatures.

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## CONVERSION FACTORS

### SI Units to Metric or English Units

| To Obtain | From | Multiply By |
|---|---|---|
| g/Mcal | ng/J | 0.004186 |
| $10^6$ Btu | GJ | 0.948 |
| Btu | gm cal | $3.9685 \times 10^{-3}$ |
| lb/$10^6$ Btu | ng/J | 0.00233 |
| ft | m | 3.281 |
| in. | cm | 0.3937 |
| $ft^2$ | $m^2$ | 10.764 |
| $ft^3$ | $m^3$ | 35.314 |
| lb | kg | 2.205 |
| Fahrenheit | Celsius | $t_F = 9/5(t_c) + 32$ |
| Fahrenheit | Kelvin | $t_F = 1.8t_K - 460$ |
| psig | Pa | $P_{psig} = (P_{pa})(1.450 \times 10^{-4}) - 14.7$ |
| psia | Pa | $P_{psia} = (P_{pa})(1.450 \times 10^{-4})$ |
| iwg (39.2 °F) | Pa | $P_{iwg} = (P_{pa})(4.014 \times 10^{-3})$ |
| $10^6$ Btu/hr | MW | 3.413 |
| GJ/hr | MW | 3.60 |

| To Obtain ppm at 3% $O_2$ of | Multiply* Concentration in ng/J by |
|---|---|
| **Natural Gas Fuel** | |
| CO | 3.23 |
| HC | 5.65 |
| NO or $NO_x$ | 1.96 |
| $SO_2$ or $SO_x$ | 1.41 |
| **Oil Fuel** | |
| CO | 2.93 |
| HC | 5.13 |
| NO or $NO_x$ | 1.78 |
| $SO_2$ or $SO_x$ | 1.28 |
| **Coal Fuel** | |
| CO | 2.69 |
| HC | 4.69 |
| NO or $NO_x$ | 1.64 |
| $SO_2$ or $SO_x$ | 1.18 |

*These conversions depend on fuel composition.
The values given are for typical fuels.

## English and Metric Units to SI Units

| To Obtain | From | Multiply By |
|---|---|---|
| ng/J | $lb/10^6$ Btu | 430 |
| ng/J | g/Mcal | 239 |
| GJ | $10^6$ Btu | 1.055 |
| m | ft | 0.3048 |
| cm | in. | 2.54 |
| $m^2$ | $ft^2$ | 0.0929 |
| $m^3$ | $ft^3$ | 0.02832 |
| kg | lb | 0.4536 |
| Celsius | Fahrenheit | $t_c = 5/9\ (t_F - 32)$ |
| Kelvin | Fahrenheit | $t_K = 5/9\ (t_F - 32) + 273$ |
| Pa | psig | $P_{pa} = (P_{psig} + 14.7)(6.895 \times 10^3)$ |
| Pa | psia | $P_{pa} = (P_{psia})(6.895 \times 10^3)$ |
| Pa | iwg (39.2 °F) | $P_{pa} = (P_{iwg})(249.1)$ |
| MW | $10^6$ Btu/hr | 0.293 |
| MW | GJ/hr | 0.278 |

| To Obtain ng/J of | Multiply* Concentration in ppm @ 3% $O_2$ by |
|---|---|
| **Natural Gas Fuel** | |
| CO | 0.310 |
| HC | 0.177 |
| NO or $NO_x$ (as $NO_2$) | 0.510 |
| $SO_2$ or $SO_x$ | 0.709 |
| **Oil Fuel** | |
| CO | 0.341 |
| HC | 0.195 |
| NO or $NO_x$ (as $NO_2$) | 0.561 |
| $SO_2$ or $SO_x$ | 0.780 |
| **Coal Fuel** | |
| CO | 0.372 |
| HC | 0.213 |
| NO or $NO_x$ (as $NO_2$) | 0.611 |
| $SO_2$ or $SO_x$ | 0.850 |

*These conversions depend on fuel composition.
The values given are for typical fuels.

# SECTION 1.0

# INTRODUCTION

The objective of this study was to determine the effect of boiler conditions and coal ash compositions on the sulfur retention characteristics of different eastern and western coals. To this end the results of field tests on ten industrial sized coal fired boilers have been evaluated. These ten industrial boilers represented a variety of firing types ranging from mass feed stokers to pulverized coal fired boilers. In order to support the field test results, thermodynamic equilibrium calculations have been performed on four of the coals tested in the field to predict the sulfur distribution among the ash constituents at five stoichiometric ratios for a range of temperatures.

Conditions of temperature, stoichiometry, and ash composition have been identified where thermodynamic equilibrium predicts large sulfur retention in the solid ash. Whether these large retentions are attained in the field depends upon how good the contact is between the sulfur and the metal compounds within the other constraints. In addition to the contact problem, the sulfur retention is further governed by the rates of the retention reactions and the temperature/stoichiometry history of the sulfur and ash components.

In normal combustion processes, all of the fuel sulfur is converted to sulfur oxides ($SO_x$)--mostly to $SO_2$ with a small amount being further oxidized to $SO_3$. However, in some instances for the combustion of coal, the $SO_x$ emissions have been observed to be less than expected for the complete oxidation of all of the fuel sulfur. These reduced $SO_x$ emissions were greater when the coal ashes were more alkaline.

To explain these reduced $SO_x$ emissions, the boiler conditions have been reported by other researchers to have a significant influence. The $SO_x$ emissions could be related to load and percent excess oxygen by an equation of the type:

$$\text{Percent sulfur emitted} = a + b(\text{percent excess oxygen}) + c(\text{load}/100{,}000)^* \quad (1)$$

Other studies have related sulfur retention to the mineral composition of the fuels or their ashes. For boilers firing lignite, Gronhovd (Ref. 1) and his associates found the following relationship that satisfactorily correlated their data:

$$\text{Sulfur emitted as \% sulfur in coal} = 110.1 - 12.7 \frac{CaO}{Al_2O_3} - 48.1 \frac{Na_2O}{SiO_2} \quad (2)$$

For EPA Contract 68-02-1863, comprehensive measurements on ten industrial boilers were made. Fuel and ash samples were collected for analysis at recorded load and excess oxygen conditions. The fuel samples were analyzed for ultimate constituents and the ash samples for chemical composition including CaO, $Na_2O$, $Al_2O_3$, MgO, $K_2O$, and $SiO_2$.

*In all regression analyses, load was taken in pounds of steam.

## SECTION 2.0

## SULFUR RETENTION CORRELATIONS WITH BOILER CONDITIONS AND FUEL ASH COMPOSITION

### 2.1 SULFUR RETENTION STUDIES WITH BOILER CONDITIONS

Basically, the results of overall study showed that the retention of sulfur by western coal was significantly greater than the retention of sulfur by eastern coal. The overall average western coal fuel sulfur content (of coals tested) was 775 ng/J (1.81 lb $SO_2/10^6$ Btu fired) with an average fuel sulfur emitted of 79.8%. For eastern coal, the average fuel sulfur content was 2021 ng/J (4.7 lb $SO_2/10^6$ Btu fired) with an average fuel sulfur emitted of 90.4%. Table 2-1 shows the $SO_x$ emission comparison for western and eastern coals for the industrial-sized boilers.

In order to evaluate the results from sulfur emissions studies of ten industrial-sized coal-fired boilers, multiple linear regression analyses using both combustion conditions of the boiler operations and chemical composition of the fuel ashes were performed. An assumption was made that effects of load and excess oxygen were independently controllable variables.

Table 2-2 contains the data regarding the combustion conditions (i.e., percent excess oxygen and load), coal sulfur levels and measurements of sulfur oxides emitted.

For each boiler and each type of fuel, regression analyses were performed using the relationship:

Percent sulfur emitted = a + b(percent excess oxygen) + c(load/100,000)

where a is a constant, and b and c are coefficients.

Table 2-3 presents the results of these regression analyses. The correlations accounted for 16% to 100% of the data for eastern coals and for 50% to 100% of the data for western coals. Caution must be exercised in interpreting the data; for example, the Eau Claire site with eastern coal has only three data points.

TABLE 2-1. $SO_x$ EMISSION COMPARISON FOR WESTERN AND EASTERN COALS

| Test Site | Boiler Type | Coal Source (Mine) | Average Fuel Sulfur | | | Average $SO_2$ Emissions | | | Fuel Sulfur Emitted |
|---|---|---|---|---|---|---|---|---|---|
| | | | percent | ng/J (lb $SO_2/10^6$ Btu Fired) | | ppm | ng/J (lb $SO_2/10^6$ Btu Fired) | | percent |
| | | Western Coal | | | | | | | |
| Alma | PC | Montana (Sarpy Creek) | 0.96 | 880 | (2.05) | 791 | 649 | (1.51) | 73.8 |
| Stout | VG | Wyoming (Bighorn) | 0.96 | 822 | (1.92) | 681 | 559 | (1.30) | 69.6 |
| Madison | SS | Montana (Colstrip) | 0.99 | 949 | (2.21) | 1044 | 858 | (2.00) | 90.4 |
| Willmar | SS | Montana (Colstrip) | 1.15 | 1174 | (2.74) | 934 | 766 | (1.79) | 65.3 |
| Eau Claire | TG | Wyoming (Bighorn) | 0.73 | 657 | (1.53) | 695 | 570 | (1.33) | 86.8 |
| St. Johns | DG | Wyoming (Bighorn) | 0.61 | 498 | (1.16) | 592 | 486 | (1.13) | 97.5 |
| Fremont | PC | Wyoming (Hanna-Rosebud) | 1.38 | 957 | (2.23) | 1053 | 864 | (2.01) | 90.3 |
| Fremont | PC | Colorado (Walden) | 0.38 | 263 | (0.61) | 235 | 193 | (0.45) | 73.4 |
| | | Overall Average | | 775 | (1.81) | | 618 | (1.44) | 79.8 |
| | | Eastern Coal | | | | | | | |
| Alma | PC | Kentucky (River King) | 3.57 | 2800 | (6.64) | 3036 | 2491 | (5.81) | 87.0 |
| Stout | TG | Kentucky (Vogue, Seam 2) | 2.94 | 2043 | (4.76) | 2129 | 1747 | (4.07) | 85.5 |
| Willmar | SS/TG | So. Illinois (Stonefort) | 2.28 | 1567 | (3.65) | 1815 | 1489 | (3.47) | 94.0 |
| Eau Claire | VG | W. Kentucky (Vogue) | 2.87 | 1803 | (4.72) | 2363 | 1939 | (4.52) | 95.0 |
| Madison | SS/TG | W. Kentucky (Vogue) | 3.04 | 2167 | (5.05) | 2378 | 1952 | (4.55) | 90.0 |
| Fairmont | PC | So. Illinois (Sahara) | 2.13 | 1471 | (3.43) | 1628 | 1336 | (3.11) | 89.7 |
| | | Overall Average | | 2021 | (4.71) | | 1826 | (4.25) | 90.4 |

Average $SO_x$ reduction based on flue gas emission measurements = 1206 ng/J (2.81 lb $SO_2/10^6$ Btu) = 66.1%

Average $SO_x$ reduction based on fuel analysis = 1244 ng/J (2.90 lb $SO_2/10^6$ Btu) = 61.7%

VG - Vibrating Grate
TG/SS - Spreader Stoker with Travel Grate
PC - Pulverized Coal
UR - Underfed Stoker
TG - Travel Grate Stoker

## TABLE 2-2. OPERATING CONDITIONS AND SULFUR OXIDE EMISSIONS

| Site | Test No. | Load Factor % | Excess $O_2$ % | SOx ng/J | As Received: Coal Sulfur as $SO_2$ ng/J | As Received: Fly Ash Sulfur ng/J | As Received: Bottom Ash Sulfur ng/J | As Received: Heat Value J/g | As Received: Ash Content % | Measured Fuel Sulfur Emitted % | Gronhovd Prediction % | Calculated* Fuel Sulfur Emitted % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alma (PC, 29 kg/s (230x10$^3$ lb/hr) steam, Riley Stoker) | | | | | | | | | | | | |
| Eastern | 6 | 85 | 3.5 | 2561 | 2540 | - | - | 24390 | 15.03 | 101 | | 103.2 |
| | 7 | 49 | 4.7 | 2437 | 2631 | - | - | 25594 | 12.57 | 93 | | 96.2 |
| | 9 | 57 | 4.0 | 2750 | 2943 | - | - | 25013 | 14.49 | 94 | 105 | 97.8 |
| | 11 | 53 | 4.2 | 3187 | 3109 | - | - | 23519 | 18.60 | 102 | | 97.2 |
| | 14 | 89 | 3.1 | 2888 | 2704 | - | - | 24909 | 14.12 | 107 | | 104.0 |
| | 16 | 26 | 12.2 | 2109 | 2444 | - | - | 24039 | 12.78 | 86 | | 90.1 |
| | 21 | 26 | 10.6 | 2436 | 2544 | - | - | 24116 | 15.04 | 96 | | 90.5 |
| | 53 | 57 | 6.2 | 2840 | 3002 | - | - | 25229 | 13.81 | 95 | | 97.2 |
| Western | 57 | 74 | 5.7 | 754 | 806 | - | - | 21314 | 10.22 | 94 | | 81.4 |
| | 63 | 57 | 2.8 | 1242 | 1403 | - | - | 21789 | 11.71 | 89 | | 87.0 |
| | 64 | 74 | 2.9 | 619 | 808 | - | - | 19547 | 10.37 | 77 | | 82.2 |
| | 65& 66 | 57 | 4.5 | 795 | 899 | - | 43 | 20902 | 11.66 | 88 | | 86.5 |
| | 68 | 75 | 2.7 | 721 | 945 | - | 18 | 21141 | 11.82 | 76 | | 81.9 |
| | 72 | 44 | 6.7 | 1026 | 1205 | 45 | 44 | 21833 | 12.21 | 85 | 99.8 | 89.3 |
| | 73 | 41 | 5.0 | 773 | 787 | 39 | 54 | 21845 | 10.67 | 98 | | 90.6 |
| | 74 | 39 | 6.8 | 605 | 716 | 41 | 50 | 21462 | 10.48 | 84 | 96.8 | 90.6 |
| | 75 | 70 | 5.8 | 588 | 777 | 33 | 41 | 21613 | 11.19 | 76 | 96.0 | 82.6 |
| | 76 | 70 | 3.8 | 619 | 718 | 21 | - | 21961 | 11.36 | 86 | 97.4 | 83.2 |
| | 78 | 48 | 4.8 | 652 | 721 | 21 | 77 | 21590 | 12.32 | 91 | 97.4 | 88.8 |
| Stout St. U. (VG, 5.7 kg/s (45x10$^3$ lb/hr) steam, Wickes) | | | | | | | | | | | | |
| Eastern | 22 | 33 | 10.3 | 1962 | 2188 | | | 28125 | 6.5 | 90 | | 83.7 |
| | 19 | 33 | 9.9 | 1919 | 2038 | | 6 | 27953 | 7.11 | 79 | | 84.8 |
| | 27 | 53 | 11.5 | 1533 | 1860 | | | 27930 | 0.5 | 82 | | 82.8 |
| | 31 | 98 | 4.7 | 1976 | 1862 | | | 30154 | 7.25 | 106 | 109 | 105.8 |
| Western | 3 | 40 | 6.7 | 412 | 697 | | 12 | 22933 | 4.9 | 59 | | 78.3 |
| | 4 | 38 | 9.4 | 446 | 688 | | | 24118 | 4.68 | 65 | | 68.0 |
| | 8 | 58 | 6.9 | 553 | 626 | | | 22994 | 5.54 | 88 | | 80.1 |
| | 11 | 73 | 4.5 | 412 | 487 | | | 22157 | 5.06 | 85 | | 91.1 |
| | 13 | 57 | 5.7 | 436 | 425 | | | 22111 | 4.9 | 103 | | 84.3 |
| | 14 | 36 | 9.3 | 584 | 722 | | | 23010 | 3.92 | 81 | 92 | 70.9 |
| | 15 | 79 | 7.5 | 708 | 1066 | | | 23024 | 7.06 | 66 | | 80.9 |
| | 36 | 67 | 6.3 | 603 | 671 | | | 24504 | 4.88 | 90 | | 83.4 |
| Eau Claire (TG, 7.6 kg/s (60x10$^3$ lb/hr) steam, Bros.) | | | | | | | | | | | | |
| Eastern | 11 | 25 | 13.2 | 2018 | 2105 | | 13 | 38674 | 6.86 | 96 | | 96.0 |
| | 20 | 38 | 10.3 | 2139 | 1938 | | | 29880 | 6.31 | 109 | | 109.0 |
| | 30 | 75 | 6.6 | 1867 | 2053 | | 6 | 27163 | 8.03 | 91 | 108 | 91.0 |
| Western | 1 | 42 | 7.2 | 526 | 558 | | 9 | 22573 | 4.42 | 94 | | 104.1 |
| | 3 | 50 | 7.1 | 423 | 364 | | 5 | 22528 | 3.46 | 116 | | 107.9 |
| | 4 | 42 | 9.75 | 468 | 566 | | | 21913 | 3.44 | 83 | | 76.0 |
| | 7 | 27 | 9.8 | 497 | 615 | | 6 | 23419 | 5.13 | 81 | 99.5 | 81.0 |
| | 10 | 55 | 10.6 | 525 | 792 | | | 21202 | 8.22 | 66 | | 71.1 |

(continued)

*Load, Excess $O_2$ Regression Analysis

TABLE 2-2 (Continued).

| Site | Test No. | Load Factor % | Excess $O_2$ % | SOx ng/J | As Received: Coal Sulfur as $SO_2$ ng/J | As Received: Fly Ash Sulfur ng/J | As Received: Bottom Ash Sulfur ng/J | As Received: Heat Value J/g | As Received: Ash Content % | Measured Fuel Sulfur Emitted % | Gronhovd Prediction % | Calculated* Fuel Sulfur Emitted % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Madison | (SS/TG, 12.6 kg/s ($100x10^3$ lb/hr) steam, B&W) | | | | | | | | | | | |
| Eastern | 11 | 60 | 10.0 | 1711 | 2119 | | 22 | 27681 | 8.79 | 81 | | 88.1 |
| | 12 | 60 | 12.0 | 1761 | 2412 | | 25 | 28090 | 8.88 | 73 | | 94.3 |
| | 14 | 90 | 7.3 | 1739 | 2195 | | 8 | 27902 | 9.6 | 79 | 109 | 73.1 |
| | 15 | 90 | 9.1 | 1924 | 2215 | | 15 | 29085 | 7.98 | 87 | | 78.7 |
| | 17 | 30 | 14.7 | 2539 | 2053 | | 5 | 28806 | 8.7 | 124 | | 109.2 |
| | 19 | 30 | 15.8 | 2431 | 2144 | | 7 | 27263 | 9.2 | 112 | | 112.6 |
| Western | 2 | 60 | 6.5 | 862 | 953 | | | 21966 | 8.26 | 91 | 99 | 99.6 |
| | 5 | 90 | 7.2 | 919 | 719 | | 60 | 20228 | 8.29 | 122 | | 131.5 |
| | 7 | 30 | 13.6 | 492 | 908 | | 26 | 20442 | 7.99 | 54 | | 69.9 |
| | 8 | 80 | 9.7 | 1070 | 817 | | 37 | 21030 | 8.12 | 131 | | 121.7 |
| | 9 | 80 | 6.2 | 1293 | 937 | | 27 | 19840 | 8.68 | 138 | | 120.6 |
| | 10 | 30 | 13.5 | 1155 | 1224 | | 20 | 20540 | 8.95 | 94 | | 69.9 |
| | 3 | 60 | 10.9 | 1481 | 1767 | | 48 | 20242 | 10.22 | 84 | 100 | 100.9 |
| Willmar | (SS/TG, 20.2 kg/s ($160x10^3$ lb/hr) steam, Detroit Stoker) | | | | | | | | | | | |
| Eastern | 26 | 66 | 8.6 | 1791 | 1644 | | | 29182 | 8.65 | 109 | 108 | 103.5 |
| | 28 | 78 | 6.5 | 1492 | 1461 | | | 29133 | 8.22 | 102 | | 102.4 |
| | 30 | 52 | 10.0 | 1431 | 1455 | | | 28978 | 8.25 | 98 | | 104.7 |
| | 31 | 48 | 8.4 | 1550 | 1448 | | | 29257 | 8.43 | 107 | | 104.7 |
| | 32 | 55 | 11.9 | 1553 | 1468 | | | 29275 | 7.67 | 106 | | 104.8 |
| | 33 | 69 | 6.6 | 1541 | 1492 | | | 29341 | 8.34 | 103 | | 103.0 |
| | 34 | 83 | 5.9 | 1573 | 1570 | | | 29022 | 7.76 | 100 | | 101.9 |
| Western | 8 | 68 | 8.6 | 1031 | 1176 | | | 19340 | 9.12 | 88 | 100 | 88.0 |
| | 15 | 49 | 8.2 | 899 | 1000 | | | 20179 | 8.82 | 90 | | 90.0 |
| | 16 | 69 | 6.6 | 937 | 703 | | | 20467 | 8.37 | 133 | | 133.0 |
| Fairmont | (SS/TG, 10.1 kg/s ($80x10^3$ lb/hr) steam, Erie City) | | | | | | | | | | | |
| Eastern | 2 | 61 | 9.1 | 1342 | 1438 | | | 29050 | 8.67 | 93 | | 89.9 |
| | 4 | 62 | 10.1 | 1396 | 1674 | | | 29248 | 9.24 | 83 | | 92.2 |
| | 5 | 61 | 8.2 | 1151 | 1732 | | | 28930 | 8.85 | 66 | | 87.9 |
| | 7 | 74 | 8.0 | 1564 | 1323 | | | 28640 | 8.69 | 118 | 108 | 91.7 |
| | 8 | 36 | 13.5 | 1442 | 1448 | | | 29253 | 8.74 | 100 | | 90.9 |
| | 9 | 78 | 6.5 | 1350 | 1425 | | 15 | 28860 | 8.11 | 95 | | 90.0 |
| | 10 | 76 | 9.8 | 1160 | 1374 | | | 29190 | 8.41 | 84 | | 96.3 |
| Western | 11 | 75 | 7.0 | 1252 | 1882 | | | 24316 | 9.14 | 67 | | 91.7 |
| | 12 | 76 | 7.0 | 1330 | 1176 | | | 25400 | 8.96 | 113 | 106 | 91.5 |
| | 14 | 57 | 8.0 | 1314 | 1412 | | 4 | 25185 | 8.17 | 93 | | 95.5 |
| | 15 | 38 | 12.9 | 1015 | 1169 | | | 25510 | 8.97 | 87 | | 89.7 |
| | 17 | 75 | 6.6 | 1222 | 1309 | | 6 | 25900 | 9.69 | 93 | | 92.7 |
| | 18 | 57 | 9.4 | 1360 | 1349 | | | 25020 | 8.92 | 101 | | 92.0 |
| | 19 | 55 | 12.4 | 1273 | 1535 | | 11 | 26686 | 10.00 | 83 | | 84.9 |
| | 20 | 42 | 14.1 | 1170 | 1355 | | | 26549 | 7.94 | 86 | | 85.0 |

*Load, Excess $O_2$ Regression Analysis

(continued)

TABLE 2-2 (Continued).

| Site | Test No. | Load Factor % | Excess $O_2$ % | SOx ng/J | As Received: Coal Sulfur as $SO_2$ ng/J | As Received: Fly Ash Sulfur ng/J | As Received: Bottom Ash Sulfur ng/J | As Received: Heat Value J/g | As Received: Ash Content % | Measured Fuel Sulfur Emitted % | Gronhovd Prediction % | Calculated* Fuel Sulfur Emitted % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| St. Johns | (SS/DG, 1.7 kg/s ($13.5 \times 10^3$ lb/hr) steam, Keeler) | | | | | | | | | | | |
| Eastern | 11 | 63 | 14.2 | 366 | 367 | | 3 | 31027 | 6.63 | 100 | | 97.0 |
| | 12 | 45 | 15.5 | 354 | 365 | | 3 | 31685 | 5.31 | 97 | | 101.3 |
| | 13 | 43 | 16.3 | 306 | 321 | | 4 | 31046 | 7.10 | 95 | 109.9 | 102.5 |
| | 14 | 43 | 15.5 | 413 | 363 | | 1 | 31343 | 5.92 | 114 | 108.6 | 101.5 |
| | 15 | 61 | 15.6 | 372 | 373 | | 1 | 32078 | 4.42 | 100 | 108.3 | 99.0 |
| | 16 | 59 | 13.40 | 351 | 380 | | | 30524 | 5.29 | 92 | 108.3 | 96.7 |
| Western | 2 | 62 | 13.7 | 392 | 565 | | 14 | 22273 | 5.52 | 63 | | 80.1 |
| | 3 | 41 | 16.3 | 508 | 504 | | - | 22173 | 4.99 | 101 | | 96.4 |
| | 4 | 43 | 16.5 | 492 | 515 | | 8 | 22459 | 5.59 | 95 | | 89.6 |
| | 5 | 42 | 15.2 | 608 | 577 | | 15 | 22484 | 5.66 | 105 | | 108.4 |
| | 6 | 43 | 17.0 | 509 | 649 | | 8 | 22786 | 5.28 | 78 | | 83.2 |
| | 8 | 65 | 13.4 | 474 | 498 | | | 24458 | 5.14 | 95 | 97 | 79.2 |
| Fremont | (PC, 20.2 kg/s ($160 \times 10^3$ lb/hr) steam, B&W) | | | | | | | | | | | |
| Western Hanna,WY | 3 | 68 | 5.4 | 987 | 1063 | 88 | | 29150 | 9.85 | 93 | 106 | 97.6 |
| | 4 | 41 | 5.3 | 1014 | 1168 | 75 | | 28771 | 10.44 | 87 | 105 | 85.2 |
| | 5 | 83 | 5.4 | 1151 | 1072 | 76 | | 29095 | 9.99 | 107 | 104 | 104.6 |
| | 6 | 73 | 4.1 | 772 | 812 | 52 | | 28578 | 7.76 | 95 | 106 | 93.5 |
| | 7 | 68 | 3.6 | 689 | 795 | 28 | | 28694 | 7.95 | 87 | 106 | 88.2 |
| Western Walden,CO | 9 | 87 | 5.5 | 251 | 221 | - | | 28020 | - | 113 | 107 | 112.3 |
| | 11 | 72 | 4.3 | 208 | 238 | 9 | | 27706 | 8.31 | 87 | | 88.9 |
| | 13 | 70 | 5.1 | 228 | - | - | | - | - | - | | |
| | 14 | 44 | 4.2 | 184 | 268 | 13 | | 28343 | 7.85 | 68.4 | | 68.7 |
| | 15 | 70 | 3.4 | 203 | 258 | 6 | | 28664 | 7.91 | 78.7 | | 78.1 |
| Waupan | (SS/TG, 3.8 kg/s ($30 \times 10^3$ lb/hr) steam, Wickes) | | | | | | | | | | | |
| Western | 1 | 54 | 13.2 | 241 | 747 | | 23 | 20063 | 8.67 | 32 | | 41.1 |
| | 2 | 52 | 11.8 | 469 | 596 | | 10 | 20121 | 7.81 | 79 | 99 | 69.6 |
| | 3 | 91 | 11.5 | 443 | 641 | | 30 | 19960 | 8.21 | 69 | 101.6 | 38.6 |
| | 5 | 91 | 11.5 | 265 | 799 | | 26 | 20520 | 8.00 | 33 | | 38.3 |
| | 6 | 90 | 11.0 | 204 | 861 | | 23 | 20186 | 8.02 | 24 | | 49.3 |
| RDF Blend | 0% | 73 | 9.73 | 227 | 817 | | 66 | 22774 | 10.55 | 28 | 93 | 27.6 |
| | 20% RDF | 75 | 9.59 | --- | 822 | | 72 | 20557 | | -- | | -- |
| | 30% RDF | 59 | 11.53 | 156 | 822 | | 83 | 19617 | | 32 | | 32.2 |
| | 40% RDF | 76 | 10.50 | 255 | 757 | | 132 | 18554 | | 28 | | 28.0 |

*Load, Excess $O_2$ Regression Analysis

TABLE 2-3. MULTIPLE REGRESSION ANALYSIS OF ALL COALS TESTED FOR EXCESS $O_2$, LOAD, AND % SULFUR

| Site | | Coal Type | a. | b. (Excess $O_2$ Coefficient) | c. (Load Coefficient) | $R^2$ Fit Correlation |
|---|---|---|---|---|---|---|
| Alma | (8) | W. Kentucky | 88.693 | - 0.275 | 7.886 | 0.621 |
| (PC) | (11) | Montana | 103.065 | - 0.282 | - 11.773 | 0.246 |
| | (5) | Montana* | 137.584 | - 6.221 | - 14.251 | 0.913 |
| Stout St. U. | (4) | W. Kentucky | 107.159 | - 2.642 | 25.035 | 0.832 |
| (TG) | (8) | Wyoming | 97.143 | - 3.686 | 32.000 | 0.250 |
| Eau Claire | (3) | W. Kentucky | 267.766 | - 10.524 | - 218.996 | 1.000 |
| (VG) | (5) | Wyoming | 169.449 | - 11.018 | 55.739 | 0.825 |
| Madison | (6) | W. Kentucky | 70.038 | 3.109 | - 21.797 | 0.607 |
| (SS) | (7) | Montana | 34.090 | 0.296 | 105.896 | 0.688 |
| Willmar | (7) | Illinois | 106.383 | 0.174 | - 4.115 | 0.091 |
| (SS) | (3) | Montana | 255.141 | - 22.318 | 22.786 | 1.000 |
| Fairmont | (7) | So. Illinois | 49.467 | 2.176 | 42.218 | 0.027 |
| (SS) | (8) | Blend | 136.478 | - 2.598 | - 43.955 | 0.076 |
| Waupun | (5) | Montana | 348.850 | - 19.446 | - 317.128 | 0.283 |
| (SS) | (4) | RDF** | 34.536 | 0.719 | - 61.502 | 1.000 |
| St. John's | (6) | Eastern | 88.617 | 1.243 | - 107.931 | 0.105 |
| (SS-DG) | (6) | Western | 400.946 | - 12.769 | - 1720.779 | 0.504 |
| Fremont | (5) | Hanna, WY | 40.679 | 4.922 | 27.942 | 0.875 |
| (PC) | (5) | Walden, CO | - 6.770 | 9.953 | 45.991 | 0.996 |

*5 high confidence points
**Refuse-derived fuel
( ) No. of data points

(SS) - Spreader Stoker
(DG) - Dumping Grate
(TG) - Traveling Grate Stoker
(PC) - Pulverized Coal
(VG) - Vibrating Grate

Figure 2-1 contains the value of $R^2$ plotted as a function of the number of data points in Table 2-3 that were used to arrive at the $R^2$ value. Above the curve drawn in this figure is the region of 95 percent confidence interval for that number of data points. It can be seen that when the sample size is small, a large absolute value of $R^2$ is required to show significant correlation.

Seven values of $R^2$ fall below the line and twelve values are above the line.

Specifically for the Alma site for five high confidence points, the regression analysis yields the relationship:

Percent sulfur emitted = 137.6 - 6.2(percent excess oxygen) - 14.3(load/100,000)

This equation accounts for 95.6% of the variations in the data.

Table 2-4 summarizes the fit correlations for all the coals and units tested. The entries indicate whether the sulfur retention increases or decreases when the percent excess oxygen is increased and when the load is increased. Also at the bottom of Table 2-4, the total number of increases and decreases for each variable are shown for both eastern and western coals after low confidence data as well as the Waupun Refused-Derived Fuel data were eliminated. Thirty percent of the data were removed due to low confidence factors. The conclusions were that, for boilers tested, a greater sulfur retention tendency was exhibited at higher excess oxygen and a tendency for less sulfur retention at higher loads. The same overall trends held for both eastern and western coals.

More specifically for the different types of boilers, two pulverized coal-fired boilers exhibited opposing sulfur retention behavior with respect to load and excess oxygen. A unit-by-unit analysis of the stoker data did not reveal an explicit explanation of the different sulfur retention behavior between units.

Figures 2-2 through 2-11 represent the relationships using the coefficients developed in the regression analyses as shown in Table 2-3. In these figures only normal boiler operating conditions are used. The original assumption regarding variation of the boiler conditions must be reassessed. The sulfur retention behavior may have been artifically attributed to the boiler conditions as independent variables by the formulation of the terms of the regression analyses as well as the scarcity of data. In most cases, as the boiler

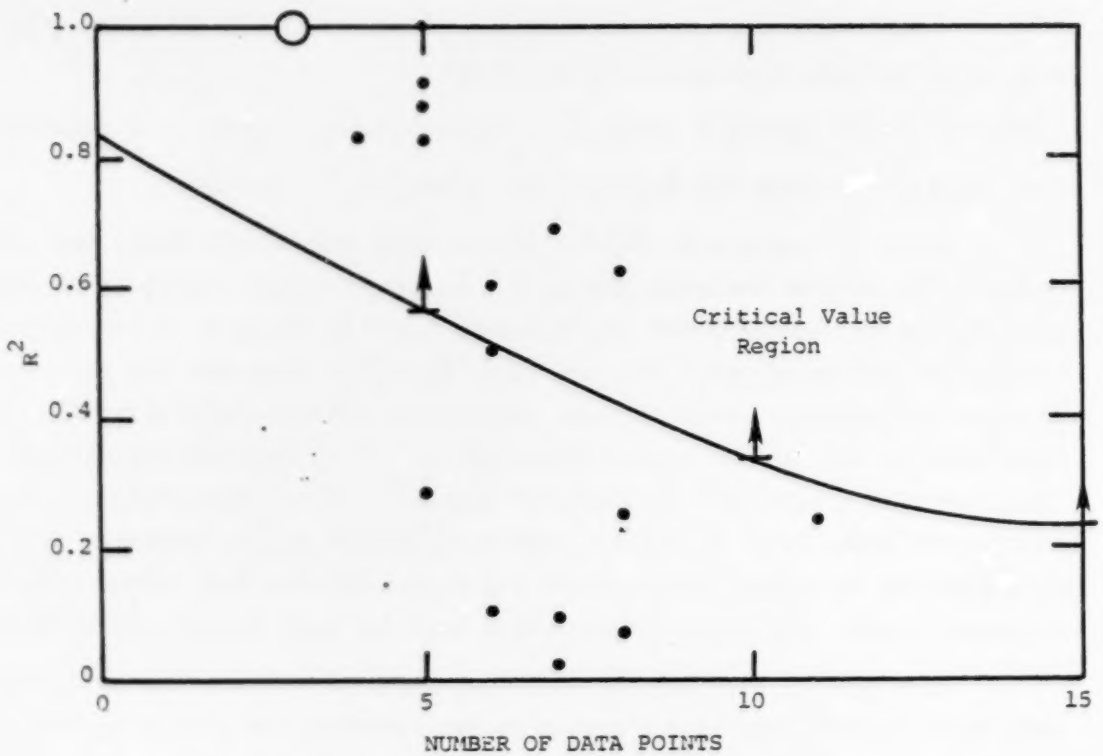


Table 2-1. $R^2$ vs. number of data points.

TABLE 2-4. SULFUR OXIDE RETENTION WITH BOILER CONDITION VARIATION

| Site<br>Boiler Type[§]<br>Boiler Capac. ($10^3$ lb/hr) | Sulfur Retention<br>Increase $O_2$ | Sulfur Retention<br>Increase Load | $R^2$ Correlation |
|---|---|---|---|
| Alma $PC_{230}$ | | | |
| Eastern | Up | Down | 0.62 |
| Western | Up | Up | 0.91[†] |
| Western | Up | Up | 0.25* |
| Stout $TG/SS_{45}$ | | | |
| Eastern | Up | Down | 0.83 |
| Western | Up* | Down* | 0.25* |
| Eau Claire $VG_{60}$ | | | |
| Eastern | Up | Up | 1.00 |
| Western | Up | Down | 0.83 |
| Madison $SS_{100}$ | | | |
| Eastern | Down | Up | 0.61 |
| Western | Down | Down | 0.69 |
| Willmar $SS_{160}$ | | | |
| Eastern | Down* | Up* | 0.09* |
| Western | Up | Down | 1.00 |
| Fairmont $SS_{80}$ | | | |
| Eastern | Up* | Down* | 0.027* |
| Western | Up* | Up* | 0.076* |
| Waupun $SS_{30}$ | | | |
| RDF | Down | Up | 1.000 |
| Western | Up* | Up* | 0.28* |
| St. Johns $DG/SS_{14}$ | | | |
| Eastern | Down* | Up* | 0.10* |
| Western | Up | Up | 0.50 |
| Fremont $PC_{160}$ | | | |
| Eastern | Down | Down | 0.88 |
| Western | Down | Down | 1.00 |
| Totals | 4 Down 7 Up | 6 Down 4 Up | |
| Eastern | (2 Down) (3 Up) | (3 Down) (2 Up) | |
| Western | (2 Down) (4 Up) | (3 Down) (2 Up) | |

Conclusion: Retention Increases With Increased $O_2$
Retention Decreases with Increased Load.

*Eliminated from totals due to blended coal supply

†5 high confidence points

§Boiler Type:
VG - Vibrograte Stoker
TG/SS - Traveling Grate Stoker
SS - Spreader Stoker
PC - Pulverized Coal
DG/SS - Dumping Grate Spreader

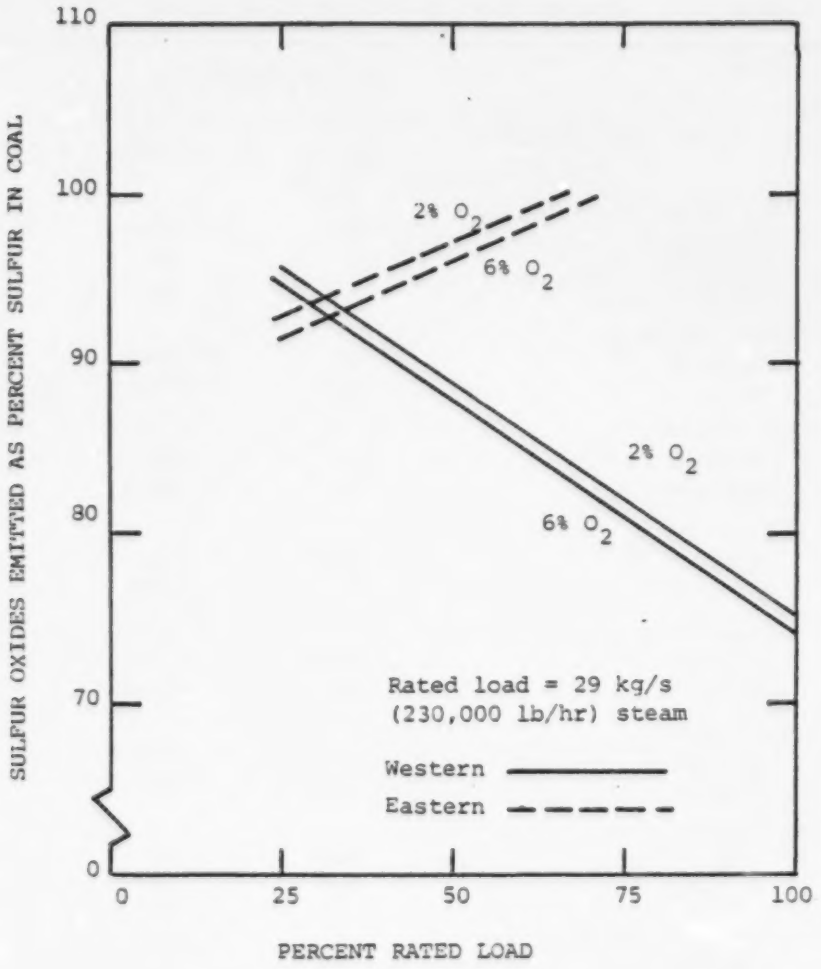


Figure 2-2. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), Alma Unit 3.

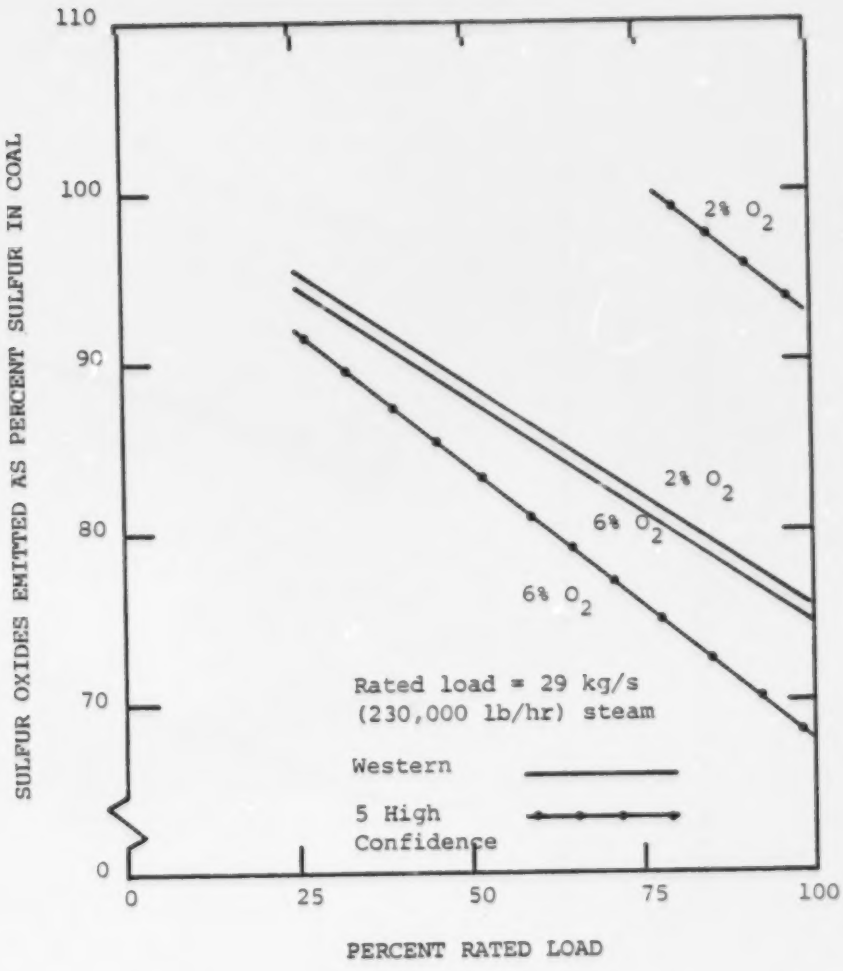


Figure 2-3. Percent sulfur oxides emitted vs. percent rated load (at different excess oxygen levels), Alma Unit 3.

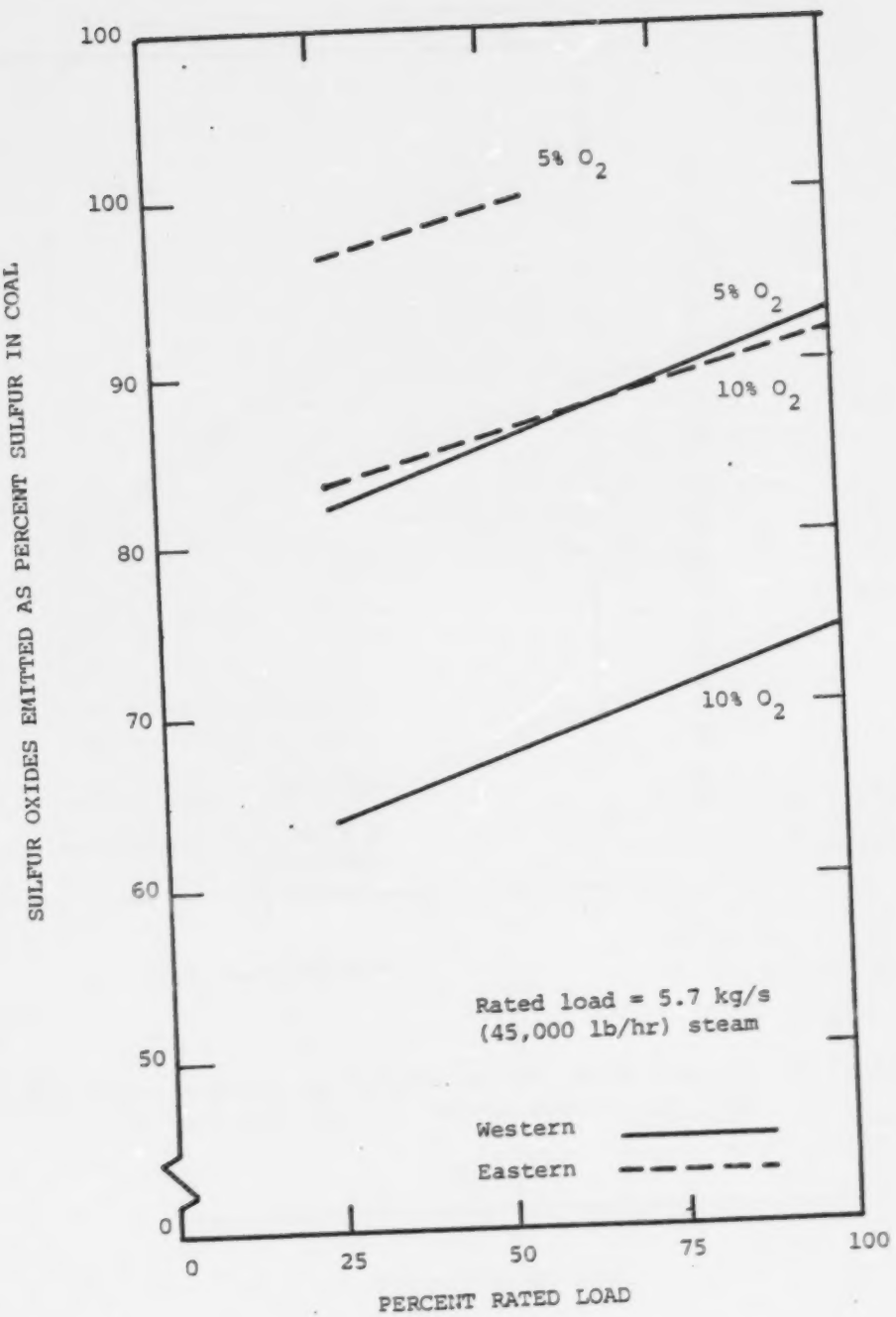


Figure 2-4. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), University of Wisconsin, Stout.

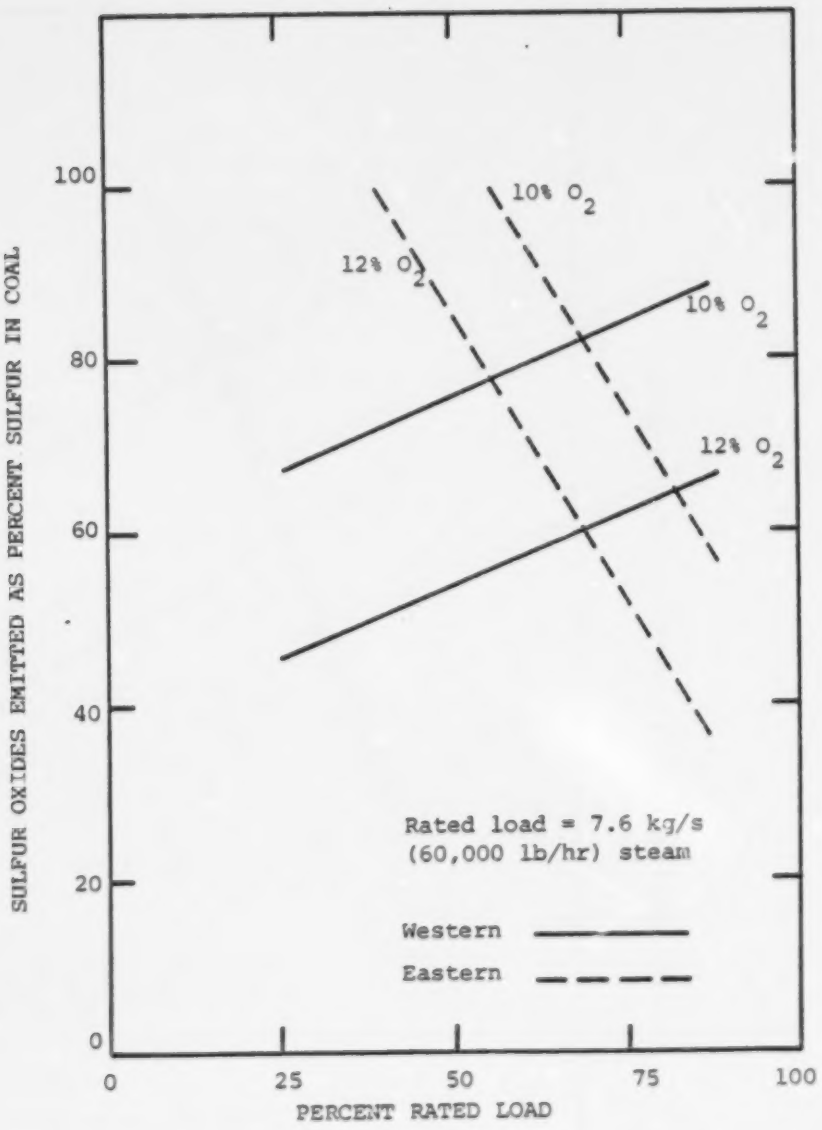


Figure 2-5. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), University of Wisconsin, Eau Claire.

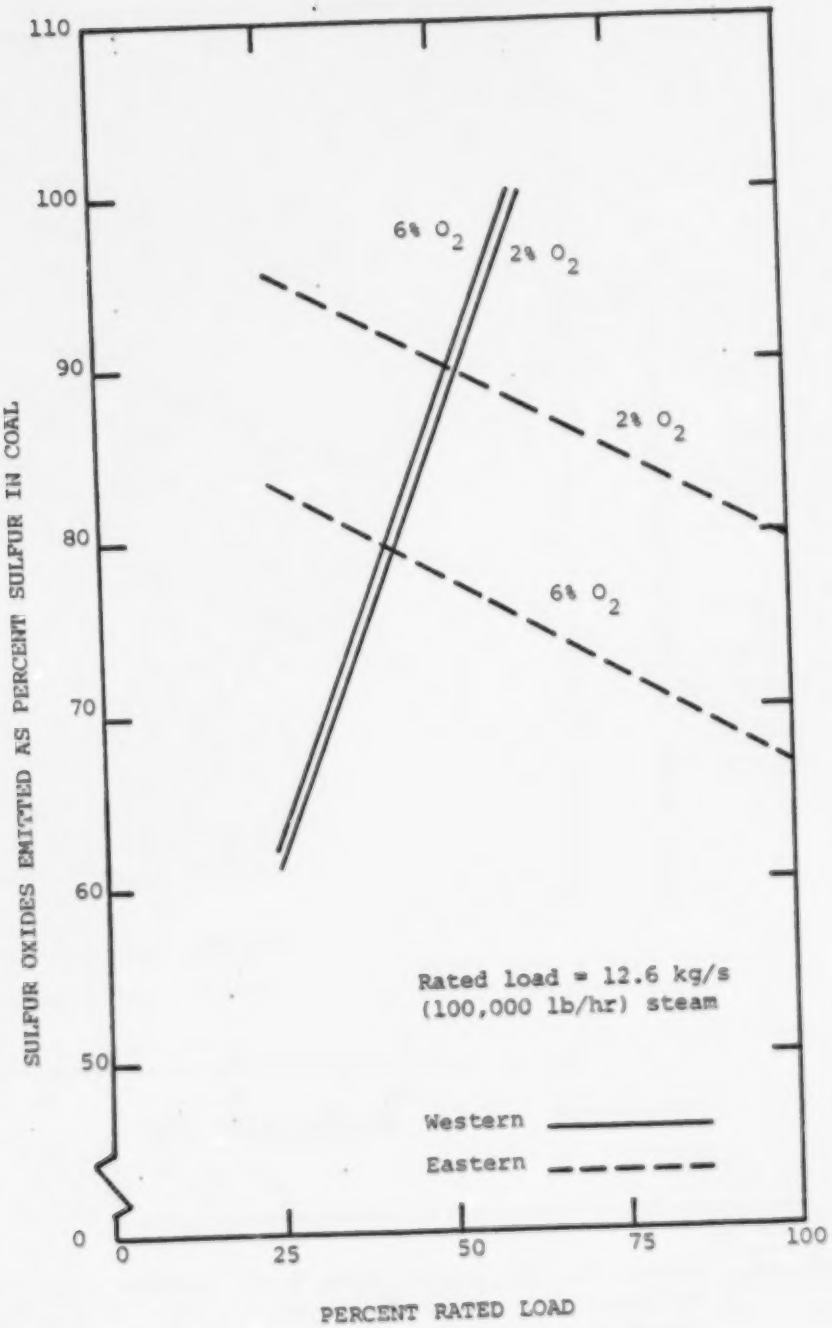


Figure 2-6. Percent sulfur oxides emitted vs. percent rated load (at different excess oxygen levels), University of Wisconsin, Madison, Unit 2.

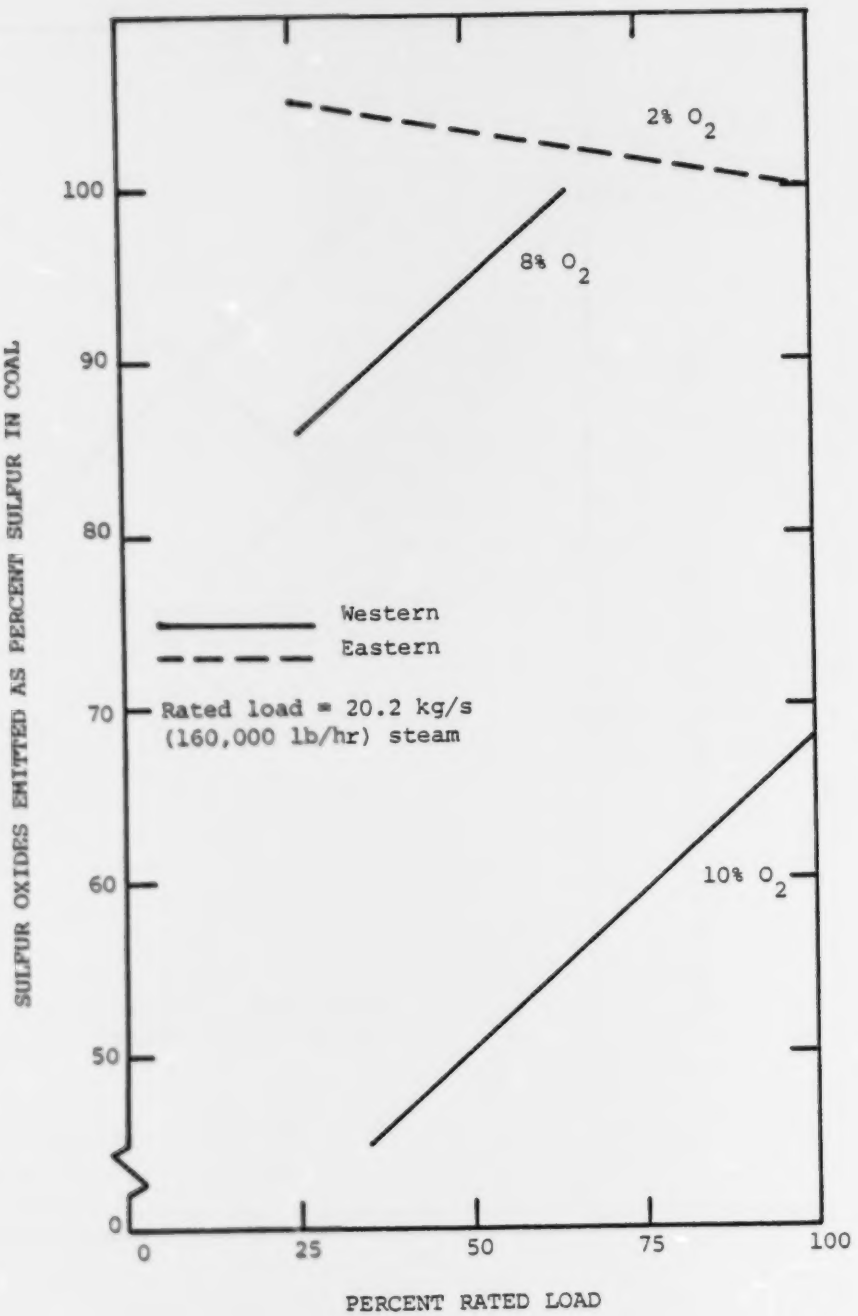


Figure 2-7. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), Willmar Unit 3.

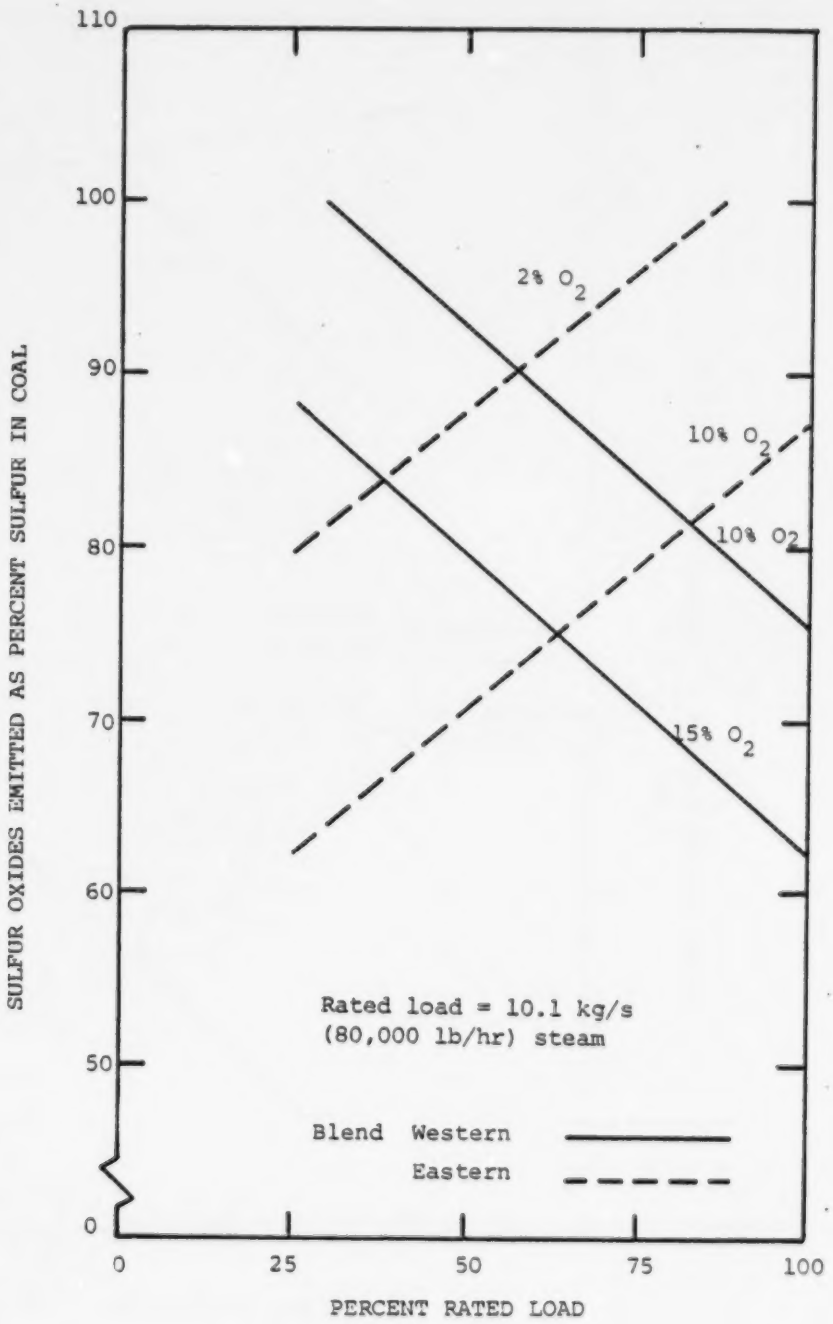


Figure 2-8. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), Fairmont Unit 3.

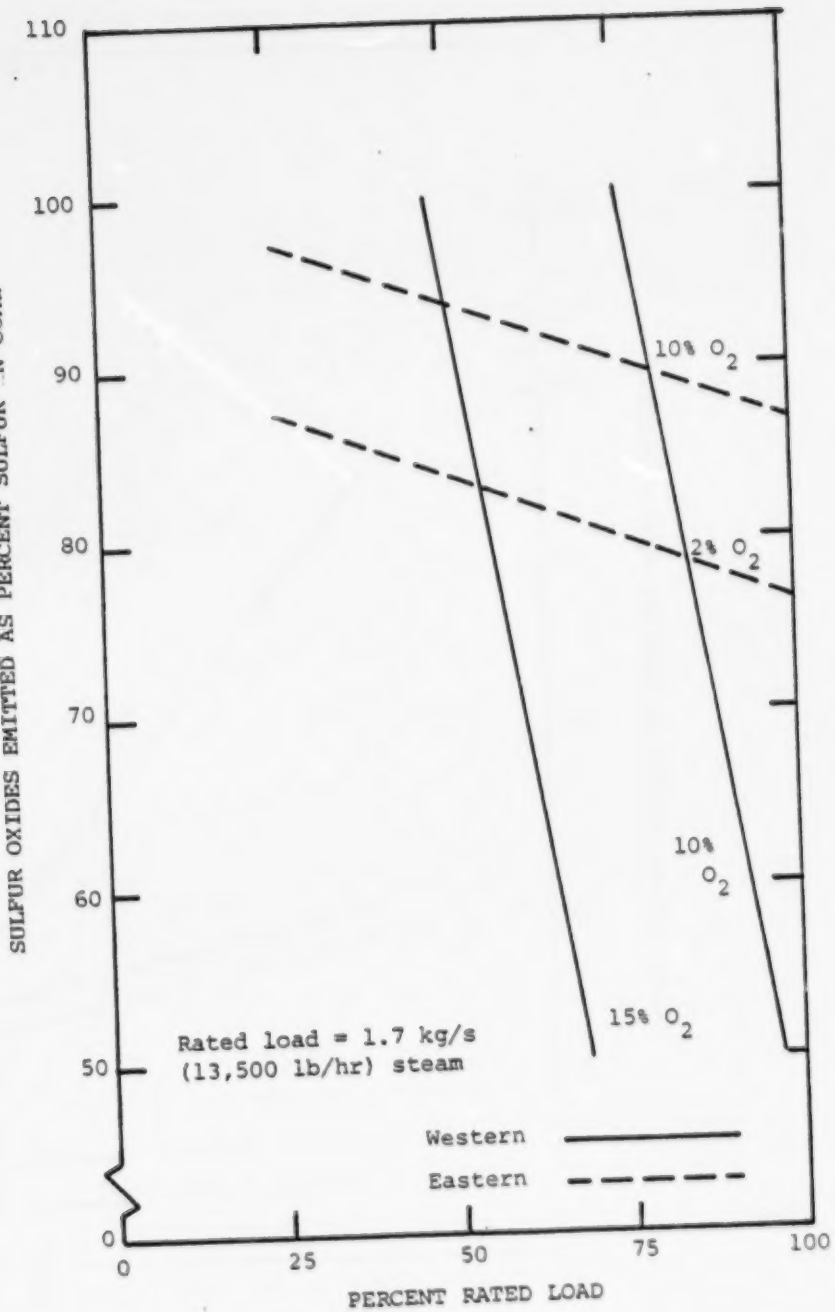


Figure 2-9. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), St. John's Unit 2.

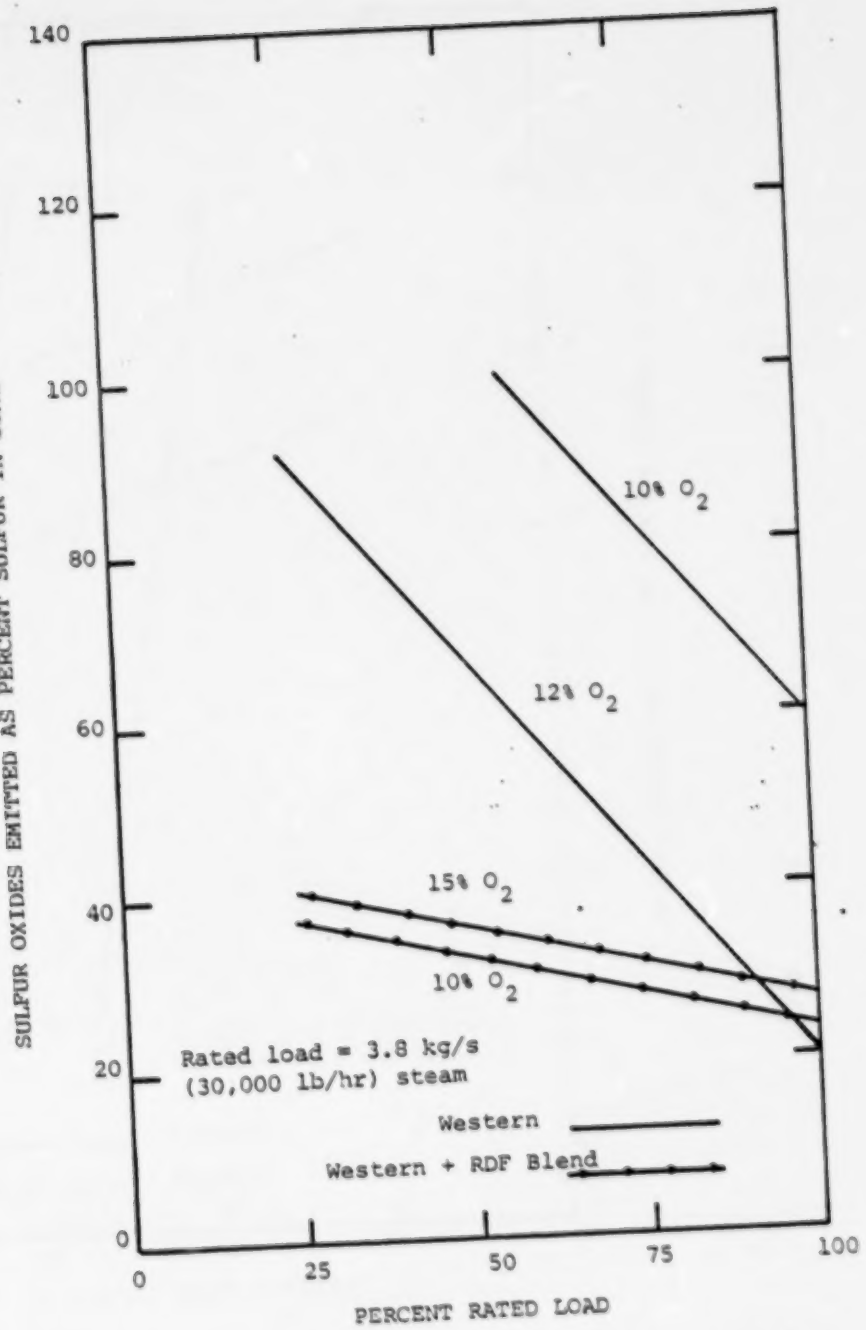


Figure 2-10. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), Waupun Unit 3.

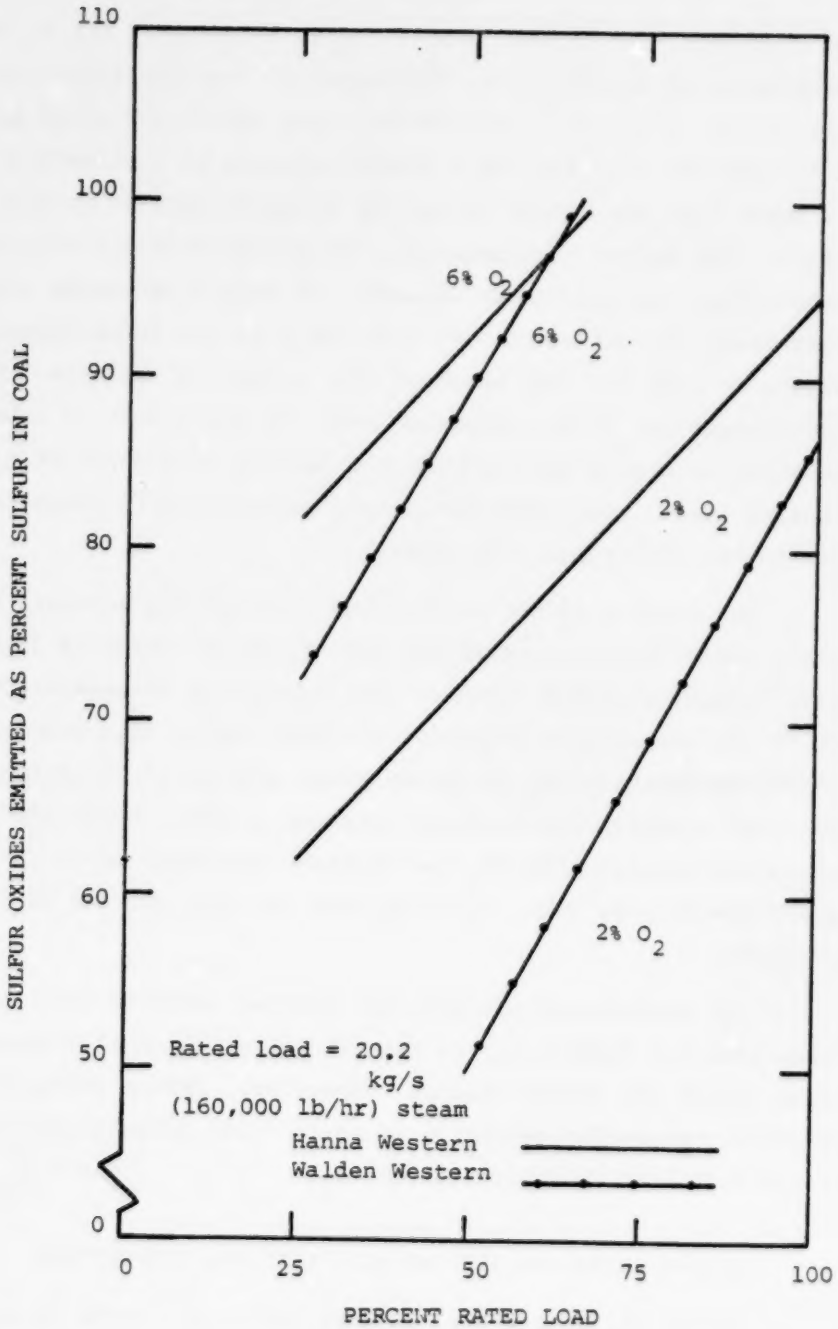


Figure 2-11. Percent sulfur oxides emitted vs. percent rated load (at different percent excess oxygen levels), Fremont Unit 6.

load increased, the percent excess oxygen decreased. Due to fan capacity limitations, it was generally impossible to vary the excess oxygen at high boiler loads. At lower loads changing the excess air could disrupt the fuel bed in a stoker unit and could lead to smoking in a pulverized-coal boiler. This meant that the excess oxygen was strongly coupled to the load for most boilers. The method of formulating the linear multiple regression analysis relationships, in the manner assumed, may have given undue weighting to the boiler load. It has been noted that the bulk gas temperature does not change drastically over the load range of most industrial boilers. The derived relationships for sulfur retention could be the result of lower operating excess air at higher load and not the derived dependence of sulfur retention on boiler load. Additional data would unquestionably increase the confidence level in the trends and conclusions.

The results of the equilibrium calculations indicate that if kinetic factors and/or mixing factors are not important, which is doubtful, then the sulfur retention should increase with decreasing temperature below about 2500 °F for all stoichiometric conditions. Below this temperature there is significant retention as condensed phase species if the metals are present in sufficient quantities to combine with the sulfur. Above 2500 °F the sulfur species are gaseous with $SO_2$ the dominant component at 75, 100, 125 and 150 percent theoretical air. At 50 percent air $H_2S$, SO, and SH share the bulk of the sulfur.

The equilibrium calculations further indicate that increasing the theoretical air (excess $O_2$) in the oxidizing region at a given temperature should reduce the sulfur emitted. Therefore, from a thermodynamic equilibrium viewpoint, the sulfur retention would increase with decreasing temperature and increase with increasing excess $O_2$.

## 2.2 SULFUR RETENTION STUDIES WITH FUEL ASH COMPOSITION

At two pulverized coal boilers which were fired on western coal, comprehensive analyses on the fuel ashes were completed for five individual test conditions as presented in Table 2-5. These sites were Alma with a maximum load of 29 kg/s (230,000 lb/hr) which was burning a Montana (Sarpy Creek) coal and Fremont with a maximum load of 20.2 kg/s (160,000 lb/hr) which was burning a Wyoming (Hanna-Rosebud) coal.

TABLE 2-5. WESTERN COAL ASH ANALYSIS

| Site (Coal)/ Test No. | Load kg/s | Load ($10^3$ lb/h) | Excess $O_2$ (%) | CaO (%) | $Na_2O$ (%) | MgO (%) | $Al_2O_3$ (%) | $SiO_2$ (%) | Meas. Sulfur Emitted, % | ln (Meas.% Sulfur Emitted) |
|---|---|---|---|---|---|---|---|---|---|---|
| Alma (Sarpy Creek, MO) | | | | | | | | | | |
| 72 | 12.75 | (101) | 6.7 | 11.32 | 2.08 | 2.12 | 18.21 | 41.96 | 85 | 4.443 |
| 74 | 11.36 | (90) | 6.8 | 13.50 | 2.71 | 2.40 | 17.14 | 39.68 | 84 | 4.431 |
| 75 | 20.33 | (161) | 5.8 | 15.20 | 3.08 | 2.84 | 19.18 | 37.17 | 76 | 4.331 |
| 76 | 20.33 | (161) | 3.8 | 13.52 | 2.63 | 2.60 | 18.07 | 40.13 | 86 | 4.454 |
| 78 | 13.89 | (110) | 4.8 | 13.50 | 2.57 | 2.60 | 18.07 | 38.91 | 91 | 4.511 |
| Fremont (Hanna-Rosebud, WY) | | | | | | | | | | |
| 3 | 17.55 | (139) | 5.4 | 6.77 | 0.28 | 2.16 | 20.85 | 48.27 | 93 | 4.533 |
| 4 | 14.52 | (115) | 5.3 | 7.50 | 0.48 | 1.92 | 19.24 | 50.08 | 87 | 4.466 |
| 5 | 14.14 | (112) | 5.4 | 7.72 | 0.41 | 2.38 | 18.91 | 47.54 | 107 | 4.673 |
| 6 | 8.84 | (70) | 4.1 | 4.70 | 0.42 | 1.90 | 15.02 | 61.43 | 95 | 4.554 |
| 7 | 14.14 | (112) | 3.6 | 4.27 | 0.34 | 1.80 | 13.37 | 62.90 | 87 | 4.466 |

As shown in Table 2-6, multiple regression analyses were performed evaluating the dependence of percent sulfur emitted on the fuel ash composition and boiler conditions. The correlations were shown to account for 17 to 98% of the variation of the percent fuel sulfur emitted for the Alma data and for 14 to 92% of the variation of the percent fuel sulfur emitted. In 7 out of 14 relationships assessed, the sign of the coefficients were the same for both Alma and Fremont indicating that the dependence of sulfur retention were similar for those particular relationships. Tables 2-7a and 2-7b present the coefficients and $R^2$ of the various relationships assessed in this study.

Table 2-8 shows a comparison of measured percent fuel sulfur emitted and the calculated percent fuel sulfur emitted by Gronhovd's relationship and the various empirical correlations developed in this study. The plots comparing the measured and calculated percent fuel sulfur emitted for three of the fuel ash composition relationships are shown in Figures 2-12 and 2-13 (A, B and C in Table 2-8). The plots show that the relationships developed from the western coal fuel ash composition data appear to predict more closely the sulfur emitted than Gronhovd's relationship for lignite burning boilers.

## 2.3 OTHER RELATED SULFUR RETENTION PROPERTIES

The effect of Commercial Testing Laboratories' sulfur analysis procedures on sulfur retention in the sample were investigated during the course of this study. This was done in order to determine the effect of the temperature history on the sample since the laboratory procedure controls the temperature as well as provides for a longer residence time at that controlled temperature. Table 2-9 contains the results of all coal samples tested by this laboratory during the project. Two points become evident. First, there was significant sulfur retention under the laboratory ashing condition at 700-750 °C and secondly, the occurrence of lime increased this retention on the average by some 45 percentage points from 7.7% retention for eastern coal samples to 53.1% retention for western coal samples. It is significant that the calcium content of western coal was higher than the others and that the western coal showed correspondingly greater sulfur retention.

TABLE 2-6. MULTIPLE REGRESSION ANALYSIS FORMULATIONS ASSESSED FOR FUEL ASH COMPOSITION AND BOILER CONDITIONS

A. RELATIONSHIPS OF TYPE $Y = a + bX + cZ$

I Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ Al_2O_3] + c[\%\ Na_2O/\%\ SiO_2]$

II Percent Sulfur Emitted = $a + b[\%\ CaO] + [\%\ Na_2O]$

III Percent Sulfur Emitted = $a + b[\%\ Na_2O/\%\ CaO] + c[Load/10^5]$

IV Percent Sulfur Emitted = $a + b[\%\ Na_2O/\%\ CaO] + c[Excess\ Oxygen]$

V Percent Sulfur Emitted = $a + b[\%\ CaO] + c[MgO]$

VI Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ MgO]$

VII Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ MgO] + c[Excess\ Oxygen]$

VIII Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ MgO] + c[Load/10^5]$

IX Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ MgO] + c[(Excess\ Oxygen \times 10^5)/Load]$

X Percent Sulfur Emitted = $a + b[\%\ CaO/\%\ MgO] + c[\%\ MgO/\%\ SiO_2]$

B. RELATIONSHIPS OF TYPE $Y = A X e^{BZ}$ or $\ln Y = a + b \ln X + c Z$

XI Percent Sulfur Emitted = $A\ [\%\ CaO/\%\ MgO]\ e^{[B\ Load/10^5]}$

XII Percent Sulfur Emitted = $A\ [\%\ CaO/\%\ MgO]\ e^{[(B\ Excess\ Oxygen \times 10^5)/Load]}$

XIII Percent Sulfur Emitted = $A\ [(\%\ CaO \cdot \%\ SiO_2)/(\%\ Al_2O_3 \cdot \%\ MgO)]\ e^{[B\ Load/10^5]}$

XIV Percent Sulfur Emitted = $A\ [Excess\ Oxygen]\ e^{[B\ Load/10^5]}$

TABLE 2-7a. MULTIPLE REGRESSION ANALYSES FOR TWO WESTERN COALS ON TWO PULVERIZED-COAL BOILERS

Relationships for Percent Sulfur Emitted of the Form $Y = a + bX + cZ$

| Site (Coal) | I [%CaO/%$Al_2O_3$], [%$Na_2O$/%$SiO_2$] | II [%CaO], [%$Na_2O$] | III [%$Na_2O$/%CaO], Load/$10^5$ | IV [%$Na_2O$/%CaO], Excess Oxygen | V [%CaO], [MgO] | VI [%CaO/%MgO] | VII [%CaO/%MgO], Excess Oxygen | VIII [%CaO/%MgO], Load/$10^5$ | IX [% CaO/% MgO], $\left[\frac{\text{Excess Oxygen} \times 10^5}{\text{Load}}\right]$ | X [%CaO/%MgO], [%MgO/%$SiO_2$] |
|---|---|---|---|---|---|---|---|---|---|---|
| **Alma (Sarpy Creek, Montana)** | | | | | | | | | | |
| a | 67.61 | 67.21 | 177.37 | 177.66 | 111.39 | 5.2 | 123.47 | 241.65 | 250.81 | 92.98 |
| b | 39.68 | 11.67 | -460.40 | -438.58 | -6.79 | 68.3 | -6.51 | -26.01 | -33.26 | 20.16 |
| c | -745.05 | -53.28 | -3.06 | -1.43 | 25.52 | -- | -0.76 | -14.62 | 2.31 | -360.39 |
| $R^2$ | 0.611 | 0.51 | 0.59 | 0.51 | 0.41 | 0.028 | 0.13 | 0.72 | 0.45 | 0.38 |
| Fit Correlation (R) | 0.78 | 0.72 | 0.77 | 0.71 | 0.64 | 0.17 | 0.36 | 0.85 | 0.67 | 0.62 |
| **Fremont (Hanna-Rosebud, Wyoming)** | | | | | | | | | | |
| a | 48.30 | 82.94 | 74.61 | 121.66 | 23.43 | 2.37 | 101.16 | 95.64 | 81.24 | 68.88 |
| b | 188.95 | 2.25 | -121.41 | -158.40 | -2.31 | 84.72 | -24.59 | 1.28 | -3.06 | 0.91 |
| c | -2903.68 | -7.95 | 25.55 | -3.17 | 41.68 | -- | 10.82 | -5.23 | 4.21 | 637.09 |
| $R^2$ | 0.313 | 0.18 | 0.70 | 0.049 | 0.84 | 0.012 | 0.84 | 0.02 | 0.38 | 0.48 |
| Fit Correlation (R) | 0.56 | 0.43 | 0.84 | 0.22 | 0.92 | 0.18 | 0.92 | 0.14 | 0.62 | 0.69 |

TABLE 2-7b. MULTIPLE REGRESSION ANALYSES FOR TWO WESTERN COALS ON TWO PULVERIZED-COAL BOILERS

Relationships for Percent Sulfur Emitted of the Form

$Y = A \times e^{BZ}$ (or $\ln Y = a + b \ln X + c Z$)

| Site (Coal) | XI<br>[% CaO/% MgO], Load/$10^5$ | XII<br>[% CaO/% MgO] Excess Oxygen x $10^5$ / Load | XIII<br>$\frac{\%CaO \cdot \%SiO_2}{\%Al_2O_3 \cdot \%MgO}$, Load/$10^5$ | XIV<br>Excess Oxygen, Load/$10^5$ |
|---|---|---|---|---|
| Alma (Sarpy Creek, Montana) | | | | |
| a | 7.55 | 8.28 | 3.83 | 5.28 |
| b | -1.72 | -2.38 | 0.25 | -0.29 |
| c | -0.18 | 0.03 | -0.01 | -0.23 |
| $R^2$ | 0.76 | 0.52 | 0.31 | 0.96 |
| Fit Correlation (R) | 0.87 | 0.72 | 0.56 | 0.98 |
| Fremont (Hanna-Rosebud, Wyoming) | | | | |
| a | 4.53 | 4.39 | 5.78 | 4.25 |
| b | 0.07 | -0.09 | -0.45 | 0.29 |
| c | -0.07 | 0.04 | -0.22 | -0.15 |
| $R^2$ | 0.04 | 0.35 | 0.61 | 0.32 |
| Fit Correlation (R) | 0.20 | 0.59 | 0.78 | 0.57 |

TABLE 2-8. COMPARISON OF MEASURED AND CALCULATED PERCENT FUEL SULFUR EMITTED

| Site/Coal | Test No. | Fuel Sulfur Emitted | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Measured % | Calculated Based on Excess Oxygen and Load % | Calculated Based on Gronhovds Coefficient (%) (A) | Calculated Based on Relationships in Tables 2-7a & b (%) | | | | | | | | | | | | | |
| | | | | | I (B) | II (C) | III | IV | V | VI | VII | VIII | IX | X | XI | XII | XIII | XIV |
| Alma | | | | | | | | | | | | | | | | | | |
| Sarpy Creek, Montana | 72 | 85 | 89 | 100 | 86 | 89 | 90 | 87 | 89 | 96 | 84 | 88 | 89 | 87 | 88 | 89 | 87 | 84 |
| | 74 | 84 | 91 | 97 | 87 | 80 | 82 | 79 | 81 | 98 | 82 | 82 | 81 | 87 | 82 | 81 | 87 | 81 |
| | 75 | 76 | 83 | 96 | 77 | 81 | 79 | 81 | 81 | 96 | 84 | 79 | 81 | 79 | 79 | 80 | 80 | 76 |
| | 76 | 86 | 83 | 97 | 86 | 85 | 83 | 87 | 86 | 95 | 87 | 83 | 83 | 84 | 83 | 83 | 83 | 86 |
| | 78 | 91 | 89 | 97 | 85 | 88 | 86 | 87 | 86 | 95 | 86 | 99 | 88 | 84 | 91 | 89 | 84 | 91 |
| Fremont | | | | | | | | | | | | | | | | | | |
| Hanna-Rosebud, Wyoming | 3 | 93 | 98 | 106 | 93 | 96 | 97 | 98 | 98 | 92 | 97 | 92 | 90 | 98 | 92 | 90 | 98 | 93 |
| | 4 | 87 | 85 | 105 | 94 | 96 | 84 | 94 | 86 | 94 | 96 | 95 | 94 | 93 | 95 | 94 | 88 | 96 |
| | 5 | 107 | 105 | 104 | 101 | 97 | 102 | 86 | 105 | 92 | 105 | 94 | 98 | 101 | 94 | 97 | 98 | 97 |
| | 6 | 95 | 94 | 106 | 88 | 90 | 94 | 84 | 92 | 91 | 91 | 95 | 100 | 89 | 95 | 99 | 98 | 96 |
| | 7 | 87 | 88 | 106 | 83 | 81 | 92 | 97 | 89 | 90 | 89 | 93 | 88 | 88 | 92 | 88 | 86 | 86 |

(A), (B) and (C) indicate correlation coefficients used in Figures 2-12 and 2-13 that follow.

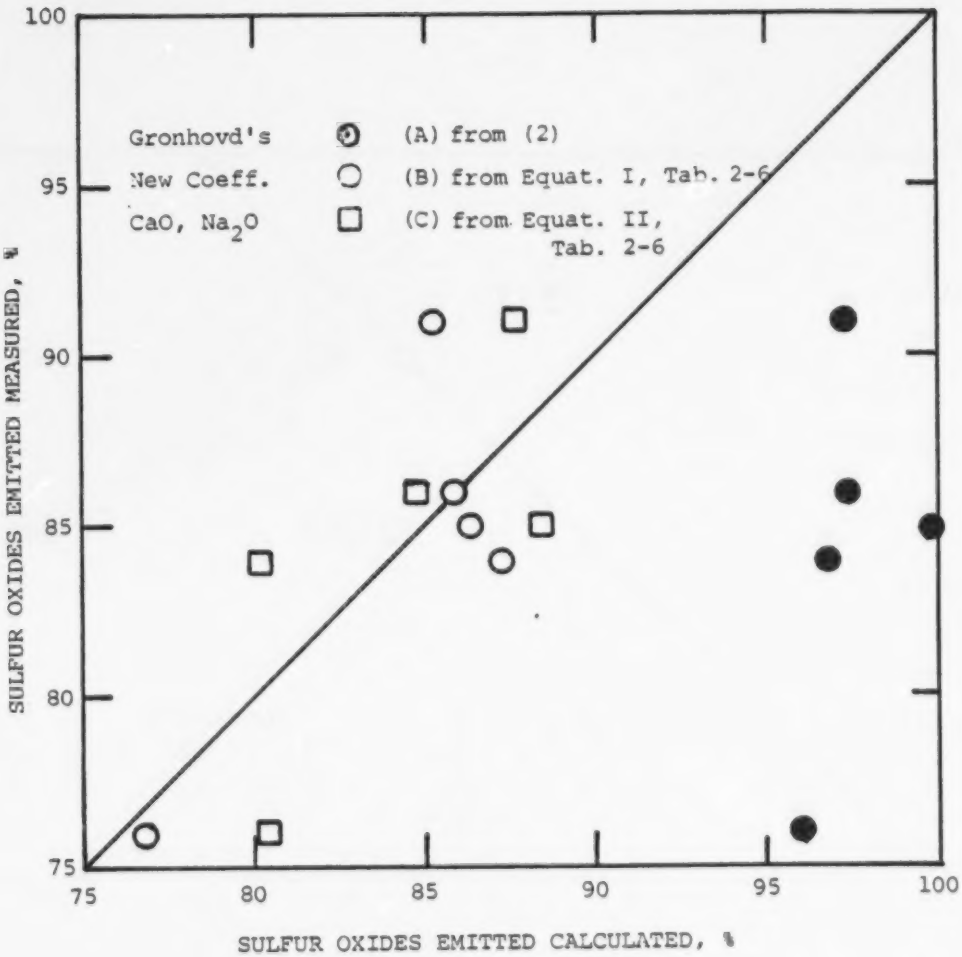


Figure 2-12. Percent sulfur oxides emitted (measured) vs. percent sulfur oxides emitted (calculated), Alma Unit 3, Sarpy Creek, Montana coal.

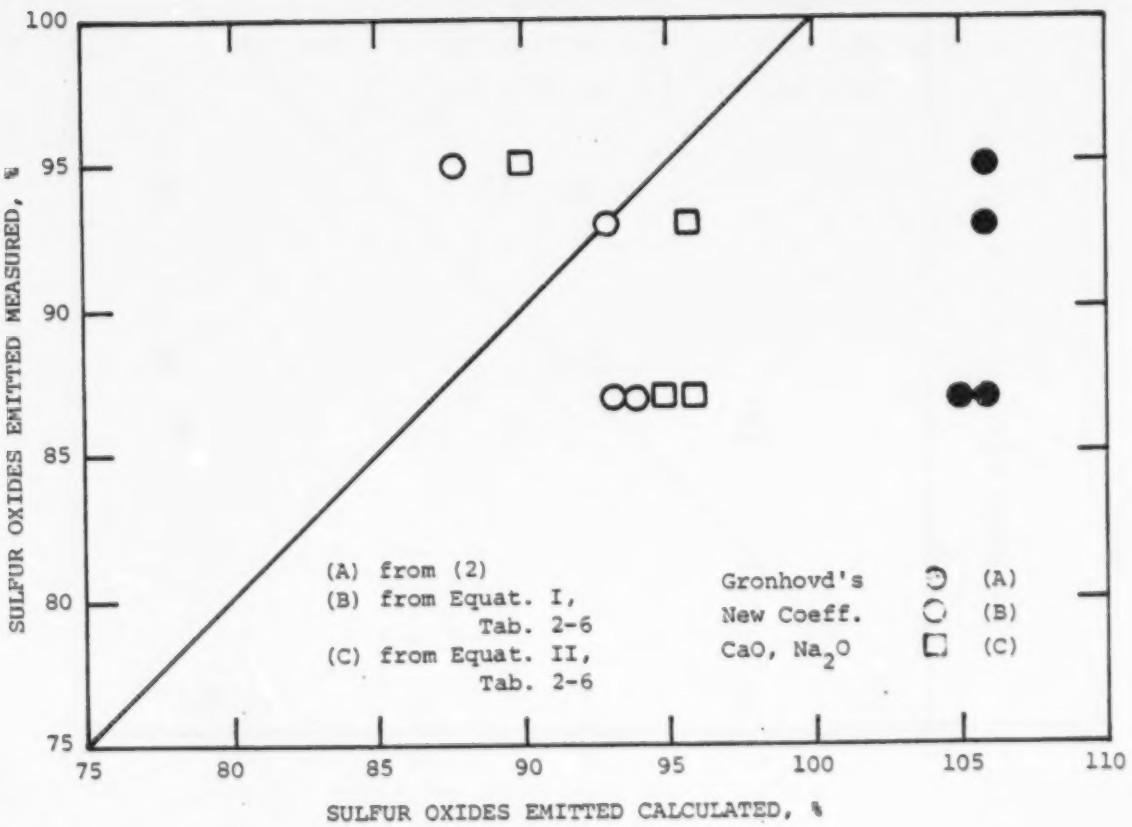


Figure 2-13. Percent sulfur oxides emitted (measured) vs. percent sulfur oxides emitted (calculated), Fremont Unit 6, Hanna-Rosebud, Wyoming coal.

TABLE 2-9. SULFUR RETENTION BY THE ASH OF THE COALS TESTED DURING LABORATORY ASHING AT 700-750 °C AND SUBSEQUENT MINERAL ANALYSIS BY COMMERCIAL TESTING

| Site/Coal Type | Test No. | Percent Retention East | West | Blend |
|---|---|---|---|---|
| Alma/E | 9 | 6.2 | | |
| Stout/W | 14 | | 33.0 | |
| Stout/E | 31 | 1.3 | | |
| Eau Claire/W | 7 | | 41.04 | |
| Eau Claire/E | 30 | 2.6 | | |
| Madison/W | 5 | | 65.4 | |
| Madison/E | 14 | 1.4 | | |
| Willmar/W | 8 | | 46.2 | |
| Willmar/E | 34 | 2.6 | | |
| Fairmont/E | 3 | 1.1 | | |
| Fairmont/E | 7 | 4.8 | | |
| Fairmont/Blend | 12 | | | 18.1 |
| Fairmont/W | -- | | 54.5 | |
| St. Johns/W | 8 | | 47.9 | |
| St. Johns/E | 16 | 15.3 | | |
| Waupun/Blend RDF | 2 | | | 75.0(W + RDF) |
| Waupun/W | -- | | 69.2 | |
| Waupun/RDF | -- | | | 123.6(RDF) |
| Fremont/Wyo | 3 | | 17.0 | |
| Fremont/Wyo | 4 | | 10.3 | |
| Fremont/Wyo | 5 | | 18.8 | |
| Fremont/Wyo | 6 | | 9.9 | |
| Fremont/Wyo | 7 | | 8.4 | |
| Fremont/Colo | 9 | | 70.8 | |
| | | Eastern Coal (Low CaO+MgO) | Western Coal (High CaO+MgO) | |
| Average Retention | | 7.7 | 53.1 | |

E = Eastern
W = Western
Wyo = Wymoing (Hanna-Rosebud)
Colo = Colorado (Walden)
RDF = Refuse-Derived Fuel

Table 2-10 presents the variations of fuel sulfur retention with calcium to sulfur ratio for a series of lignite samples with and without added lime that were evaluated in our laboratory. These experiments are of interest because it allows an experimental and theoretical comparison of the sulfur retention properties of a fuel with a known added amount of one particular metal compound. In this case the metal was calcium. Calcium is probably the most economical metal to be used in the near term to reduce sulfur. Experiments sponsored by EPA at Battelle Columbus Labs on a stoker fired boiler using lime augmented coal briquetts are currently underway. This briquetting of lime and coal technique is also being studied by the Ohio Department of Energy. Therefore it was of interest to present the results of these laboratory studies since they are relevant to the topic of sulfur retention. Figure 2-14 is the graphical representation of these variations. Commercial Testing processed these lignite samples with various molar calcium to sulfur ratios for sulfur retention under laboratory conditions. In some cases lime was added to increase the Ca/S ratio. The natural lignite had about 20% lime in the ash. The average sulfur retention of the samples with added lime was 86% while the average retention of the naturally occurring lignite was 66%.

Regression analyses of the data to assess possible relationships with exponential, logarithmic and power functions lead to the power relationship resulting in the closest agreement. The power function was of the form

$$Y = aX^b$$

where Y is the percent sulfur retention,

X is the Ca/S ratio, and

a and b are the coefficients.

The $R^2$ of fit correlation was found to be 0.784. This correlation accounted for 88.5% of the data.

The data showed that the amount of calcium in the coal does significantly affect the amount of sulfur retained in the ash under the proper (residence time and temperature) conditions. The boiler conditions dictated how close to the optimum retention the boiler would operate.

TABLE 2-10. VARIATION OF FUEL SULFUR RETENTION WITH CALCIUM/SULFUR RATIO

| Lignite Samples Ca/S | % Retention |
|---|---|
| 0.55 | 73.2 |
| 0.64 | 69.2 |
| 1.36 | 81.3 |
| 1.65 | 84.5 |
| 2.63 | 92.7 |
| 2.58 | 92.9 |
| 1.18 | 75.9 |
| 2.80 | 88.5 |
| 0.59 | 56.0 |

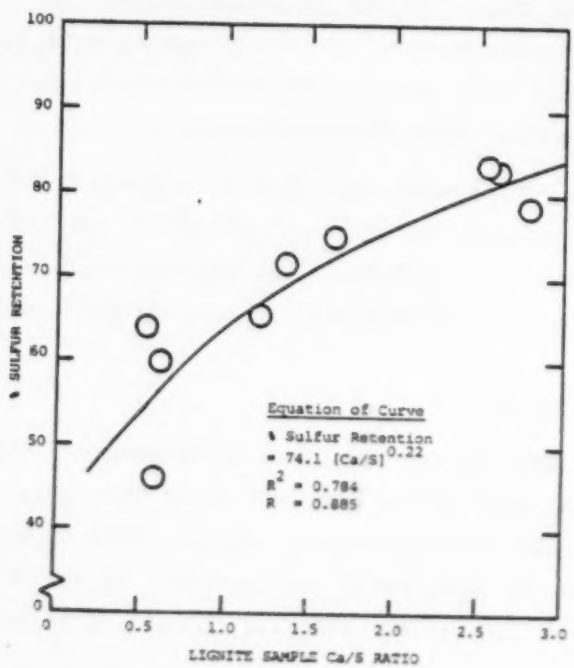


Figure 2-14. Percent sulfur retention vs. calcium to sulfur (Ca/S) ratio for lignite samples.

# SECTION 3.0

# THERMOCHEMICAL EQUILIBRIUM SULFUR DISTRIBUTIONS

## 3.1 INTRODUCTION AND BACKGROUND

The primary objective of this task was to determine, on a thermochemical equilibrium basis, the gas-phase and condensed-phase distributions of the fuel sulfur as a function of coal type, temperature and air/fuel ratio (stoichiometry). These distributions would establish the extent to which the sulfur was associated with condensed phase (liquid and solid) species which could be electrostatically precipitated from the flue gas or collected in the bottom ash.

A secondary objective was to evaluate which of the coal types investigated would be amenable to greater sulfur retention by augmentation with suitable additives. This was only a cursory evaluation and did not identify sulfur retention sensitivity to augmentation.

All calculations were performed by a generalized computer program developed by the National Aeronautics and Space Administration (NASA). This program has received wide industrial acceptance and has recently been extended specifically for greater flexibility in considering coal analyses.

## 3.2 COMPUTER PROGRAM

The computer program described in Reference 2 was used to calculate the thermochemical equilibrium composition of four coal types over ranges in both temperature and air/fuel weight ratios. This program, which has been under development for many years, can consider up to 200 distinct species of which a maximum of 100 may be condensed (liquid or solid).

The coal composition is specified as part of the input and the program searches an extensive thermochemical file to select those species which can be formed from the chemical elements present in the coal. The user can specify that up to 66 species be omitted from those selected if it is known, a priori, that these species are unimportant.

The program then starts an iterative procedure to find product mole fractions subject to the problem constraints. In this instance the temperature, pressure (one atmosphere), and elemental composition are the known constraints. The program then cycles to the next set of constrainst using the previous solution as an initial estimate of species concentrations.

At low temperature, the solution obtained may be somewhat inaccurate because of uncertainties in species thermochemical data and the assumptions that all gases are ideal and interactions among phases may be neglected.

The calculations were performed on an UNIVAC 1108 with certain key variables expressed in double precision.

## 3.3 COAL COMPOSITIONS

Table 3-1 contains the coal compositions weight percentages, on a dry basis, of the four coals investigated in the equilibrium calculations. Chlorine was omitted from lignite, augmented lignite and Pittsburgh #8, since its inclusion caused the species count to exceed the 200 limitation. This was also justifiable since its maximum concentration was 0.02% in the coal. Phosphorous pentoxide ($P_2O_5$) was not included as an ash constituent because of its low concentration. The ash metal oxide concentrations shown in Table 3-1 reflect their abundance in the coal and not in the ash.

These coals were selected to cover the range of coal types in terms of ash composition and as well as to be representative of the coals tested in the field study. The Montana coal was actually one of the test coals. The Pittsburgh coal was similar to the eastern coals tested as well as being a major steam coal. The lignite were investigated since there was laboratory experimental data available for comparison. The augmented lignite served as a case where a controlled amount of calcium had been added as well as having combustion laboratory data on this coal.

As shown, there is only a factor of 2 difference in the sulfur content of the coals, and this factor could increase to 3.5 to 4 for different eastern coals. Even more pronounced is the difference in calcium (as CaO) content among the coals, with Pittsburgh #8 being an order of magnitude less than the next lower value. Further, Pittsburgh #8 has the lowest concentrations of magnesium (as MgO) and sodium (as $Na_2O$). The impact of these low concentrations will be discussed later in more detail.

TABLE 3-1. COAL COMPOSITIONS

| Coal | Weight Percent, Dry | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | O | S | Ash | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ |
| Montana Lignite | 69.78 | 6.51 | 0.96 | 8.70 | 1.05 | 13.00 | 4.34 | 4.15 | 0.13 | 1.50 | 1.50 | 0.33 | 0.08 | 0.96 |
| Augmented Lignite | 66.41 | 4.45 | 1.31 | 17.12 | 1.00 | 9.70 | 3.72 | 1.68 | 0.12 | 0.73 | 1.98 | 0.78 | 0.04 | 0.09 |
| Pittsburgh #8 | 59.27 | 4.58 | 1.10 | 20.99 | 0.98 | 13.07 | 3.45 | 1.47 | 0.10 | 0.61 | 5.39 | 0.68 | 0.08 | 0.07 |
| | 77.45 | 5.19 | 1.51 | 6.71 | 1.84 | 7.28 | 3.59 | 1.81 | 0.08 | 1.42 | 0.15 | 0.05 | 0.11 | 0.02 |

## 3.4 COMPUTER RESULTS

A total of 160 discrete point calculations were obtained for the following conditions:

Pressure - 1 atmosphere

Temperature - 3300, 2900, 2500, 2100, 1700, 1300, 900, 500 °F

Stoichiometry - 50, 75, 100, 125, 150% theoretical air (by weight)

The calculations were performed in decreasing temperature steps in order to minimize computer time, i.e., the solutions were first obtained with the fewest number of condensed species present. Table 3-2 presents the computer output for lignite coal at 50% theoretical air. The density and mole fraction print format is interpreted as follows: 8.4421-4 = $8.4421 \times 10^{-4}$. The last part of Table 3-2 lists those species whose concentrations were less than $1 \times 10^{-6}$ (1 ppm) throughout the temperature range.

A sulfur mass balance was established for each of the 160 point calculations in order to determine which species were combined with sulfur as a function of temperature and stoichiometry. The resulting distributions were then summed by species phase, gas vs. liquid/solid.

The results of the sulfur mass balance for each coal are presented in Tables 3-3 to 3-6. Only those values greater than, or equal to, 0.1% are shown in order to improve their readability. The values in Tables 3-3 to 3-6 represent the weight percentage of the total sulfur associated with each species. For example, in Table 3-3 at 50% theoretical air and 3300 °F, the sulfur contained in the COS molecule represents 3.6% of the total sulfur mass in the system. Similarly, $H_2S$ contains 36.3% of the total sulfur, etc. Further, all the sulfur is combined with gas-phase species. Conversely, at 500 °F 97.4% (48.0 + 2.5 + 46.9) of the sulfur is associated with condensed species (L - liquid, S - solid).

Table 3-7 was prepared by summing up the sulfur content of the condensed species for each of the 160 discrete point calculations. As anticipated, low temperatures favor sulfur retention by condensed species, i.e., except for Pittsburgh #8 over 90% of the sulfur is associated with condensed species for temperatures of 900 °F and less.

TABLE 3-2. COMPUTER OUTPUT FOR LIGNITE AT 50% THEORETICAL AIR

09/15/78 10:52:11 COAL 0130AA25 000130 9 100 DATE 091578 PAGE 8

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED

TEMPERATURE AND PRESSURE

CASE NO. 12

| | CHEMICAL FORMULA | | | | | | | | WT FRACTION (SEE NOTE) | ENERGY CAL/MOL | STATE | TEMP DEG K | DENSITY G/CC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FUEL | C 1.00000 | H .79870 | N .01690 | S .00570 | O .19350 | | | | .902982 | .000 | | .00 | .0000 |
| FUEL | SI 1.00000 | O 2.00000 | | | | | | | .037203 | .000 | | .00 | .0000 |
| FUEL | AL 2.00000 | O 3.00000 | | | | | | | .016812 | .000 | | .00 | .0000 |
| FUEL | TI 1.00000 | O 2.00000 | | | | | | | .001154 | .000 | | .00 | .0000 |
| FUEL | FE 2.00000 | O 3.00000 | | | | | | | .008673 | .000 | | .00 | .0000 |
| FUEL | CA 1.00000 | O 1.00000 | | | | | | | .023369 | .000 | | .00 | .0000 |
| FUEL | MG 1.00000 | O 1.00000 | | | | | | | .007790 | .000 | | .00 | .0000 |
| FUEL | K 2.00000 | O 1.00000 | | | | | | | .000960 | .000 | | .00 | .0000 |
| FUEL | NA 2.00000 | O 1.00000 | | | | | | | .001057 | .000 | | .00 | .0000 |
| OXIDANT | N 1.56180 | O .41960 | AR .00930 | C .00030 | | | | | 1.000000 | .000 | | .00 | .0000 |

O/F= 4.2373 PERCENT FUEL= 19.0938 EQUIVALENCE RATIO= 1.8211 PHI= 2.0000 REACTANT DENSITY= .0000

THERMODYNAMIC PROPERTIES

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| P, ATM | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| T, DEG K | 2089.0 | 1867.0 | 1644.0 | 1422.0 | 1200.0 | 978.0 | 756.0 | 533.0 |
| RHO, G/CC | 1.5750-4 | 1.7657-4 | 2.0060-4 | 2.3193-4 | 2.7484-4 | 3.3729-4 | 4.9848-4 | 7.3352-4 |
| H, CAL/G | 23.2 | -59.3 | -136.1 | -210.2 | -283.3 | -355.7 | -596.0 | -692.1 |
| S, CAL/(G)(K) | 2.3404 | 2.2987 | 2.2549 | 2.2065 | 2.1506 | 2.0840 | 1.8075 | 1.6603 |
| M, MOL WT | 26.998 | 27.050 | 27.061 | 27.062 | 27.062 | 27.067 | 30.923 | 32.081 |
| (DLV/DLP)T | -1.00099 | -1.00036 | -1.00003 | -1.00001 | -1.00002 | -1.00009 | -1.01272 | -1.00095 |
| (DLV/DLT)P | 1.0233 | 1.0089 | 1.0007 | 1.0001 | 1.0002 | 1.0019 | 1.2567 | 1.0201 |
| CP, CAL/(G)(K) | .3845 | .3562 | .3369 | .3313 | .3270 | .3247 | .6528 | .2984 |
| GAMMA (S) | 1.2492 | 1.2652 | 1.2792 | 1.2848 | 1.2897 | 1.2935 | 1.1665 | 1.2740 |
| SON VEL,M/SEC | 896.5 | 852.1 | 803.8 | 749.2 | 689.5 | 623.4 | 486.9 | 419.5 |

(S) = Solid

MOLE FRACTIONS

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| AL2O3(S) | 8.4421-4 | 8.4514-4 | 8.4543-4 | 8.4546-4 | 8.4548-4 | 8.4555-4 | 8.4555-4 | 8.4719-4 |
| AR | 6.9670-3 | 6.9738-3 | 6.9762-3 | 6.9765-3 | 6.9766-3 | 6.9772-3 | 6.9772-3 | 6.9907-3 |
| C(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 1.2359-1 | 1.5369-1 |
| CO | 2.4540-1 | 2.4265-1 | 2.3852-1 | 2.3311-1 | 2.2547-1 | 2.1499-1 | 1.6566-2 | 4.8387-5 |
| COS | 6.4013-5 | 1.0594-4 | 5.0240-5 | 1.8590-5 | 4.6879-6 | 6.1142-7 | 3.9398-8 | 1.6639-8 |
| CO2 | 3.7895-2 | 4.0875-2 | 4.5157-2 | 5.0615-2 | 5.8272-2 | 6.8758-2 | 1.4361-1 | 1.2962-1 |
| CAO(S) | 2.1209-3 | 1.7976-3 | 1.0292-3 | 7.2344-4 | 5.7952-4 | 5.2979-4 | 5.7580-4 | .0000 0 |
| CAOH | 2.942 -6 | 1.736 -7 | 4.548 -9 | 3.742-11 | 4.927-14 | 2.929-18 | 3.026-25 | .000 0 |
| CAO2H2(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 6.8600-4 |
| CAO2H2 | 9.569 -6 | 1.536 -6 | 1.456 -7 | 6.357 -9 | 8.131-11 | 1.261-13 | 3.061-17 | 3.757-27 |
| CAS(S) | .0000 0 | 3.3671-4 | 1.1074-3 | 1.4134-3 | 1.5573-3 | 1.6072-3 | 1.5612-3 | 1.4551-3 |
| FE | 5.208 -4 | 4.560 -5 | 1.770 -6 | 1.874 -8 | 3.515-11 | 3.656-15 | 6.920-23 | .000 0 |
| FEO(S) | .0000 0 | .0000 0 | 5.5293-4 | 5.5669-4 | 5.5697-4 | 5.5702-4 | 5.5702-4 | .0000 0 |
| FEO(L) | .0000 0 | 5.0145-4 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 |

TABLE 3-2. (Continued)



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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| FE02H2 | 2.538 -5 | 9.230 -6 | 2.243 -6 | 2.553 -7 | 1.212 -8 | 1.272-10 | 6.426-13 | 7.121-19 | | |
| FE3O4(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 1.8603-4 | | |
| H | 7.300 -4 | 1.576 -4 | 2.250 -5 | 1.788 -6 | 5.649 -8 | 3.778-10 | 8.290-14 | 9.273-21 | | |
| H2 | 6.4144-2 | 6.6778-2 | 7.0555-2 | 7.5973-2 | 8.3634-2 | 9.4147-2 | 4.5676-2 | 3.1254-3 | | |
| H2O | 4.7897-2 | 4.5403-2 | 4.2180-2 | 3.7023-2 | 2.9476-2 | 1.8969-2 | 6.7465-2 | 1.0962-1 | | |
| H2S | 4.5112-4 | 8.1685-4 | 4.3284-4 | 1.8302-4 | 5.4036-5 | 8.3603-6 | 3.1908-6 | 2.4160-5 | | |
| K | 8.634 -5 | 7.983 -5 | 6.927 -5 | 5.345 -5 | 3.258 -5 | 1.269 -5 | 1.329 -9 | 4.571-22 | | |
| KOH | 1.804 -5 | 2.465 -5 | 3.525 -5 | 5.107 -5 | 7.192 -5 | 8.874 -5 | 7.470 -7 | 2.657-16 | | |
| K2O2H2 | 2.172-13 | 1.489-12 | 1.617-11 | 3.051-10 | 1.242 -8 | 1.552 -6 | 1.380 -7 | 6.934-21 | | |
| K2SO4(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 5.1754-5 | 5.2366-5 | | |
| HG | 6.486 -5 | 2.736 -6 | 4.692 -8 | 2.286-10 | 1.522-13 | 3.635-18 | 7.030-27 | .000 0 | | |
| HGCO3(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 9.5578-4 | | |
| HGO(S) | 7.6560-4 | 8.3867-4 | 8.4259-4 | 8.4273-4 | 8.4275-4 | 8.4282-4 | 8.4282-4 | .0000 0 | | |
| HGOH | 7.094 -6 | 4.204 -7 | 1.113 -8 | 9.348-11 | 1.276-13 | 8.088-18 | 9.417-25 | .000 0 | | |
| HGO2H2 | 3.758 -6 | 5.729 -7 | 5.108 -8 | 2.071 -9 | 2.411-11 | 3.292-14 | 6.621-18 | 4.442-27 | | |
| HGTI2O5(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 3.7109-5 | | |
| HG2TIO4(S) | .0000 0 | 7.4039-5 | 7.4065-5 | 7.4068-5 | 7.4069-5 | 7.4075-5 | 7.4075-5 | .0000 0 | | |
| HG2TIO4(L) | 7.3913-5 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | | |
| NO | 7.902 -6 | 6.917 -7 | 3.074 -8 | 5.104-10 | 1.806-12 | 4.637-16 | 1.632-20 | 7.689-29 | | |
| N2 | 5.8739-1 | 5.8797-1 | 5.8817-1 | 5.8819-1 | 5.8821-1 | 5.8824-1 | 5.8825-1 | 5.8939-1 | | |
| NA | 1.631 -4 | 1.599 -4 | 1.544 -4 | 1.449 -4 | 1.265 -4 | 2.890 -5 | 4.128-10 | 4.242-21 | | |
| NACN | 2.315 -9 | 6.783 -9 | 2.670 -8 | 1.635 -7 | 1.949 -6 | 2.171 -5 | 8.306-10 | 1.973-20 | | |
| NAOH(L) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 1.0111-4 | 1.7492-4 | .0000 0 | | |
| NAOH | 1.127 -5 | 1.463 -5 | 2.021 -5 | 2.960 -5 | 4.632 -5 | 2.319 -5 | 1.480 -8 | 5.338-17 | | |
| NA2SO4(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 8.7635-5 | | |
| OH | 6.283 -5 | 8.063 -6 | 5.839 -7 | 1.831 -8 | 1.535-10 | 1.354-13 | 2.107-17 | 7.622-25 | | |
| S | 8.039 -5 | 1.688 -5 | 5.715 -7 | 6.650 -9 | 1.451-11 | 1.864-15 | 2.103-20 | 3.945-27 | | |
| SH | 2.400 -4 | 1.330 -4 | 1.551 -5 | 9.039 -7 | 1.772 -8 | 5.402-11 | 6.096-14 | 2.363-17 | | |
| SO | 3.383 -4 | 7.736 -5 | 2.898 -6 | 3.725 -8 | 8.969-11 | 1.235-14 | 2.852-18 | 9.015-23 | | |
| SO2 | 4.323 -4 | 1.264 -4 | 6.470 -6 | 1.218 -7 | 4.825-10 | 1.296-13 | 1.635-15 | 5.627-17 | | |
| S2O | 1.737 -6 | 8.765 -7 | 2.227 -8 | 1.666-10 | 1.852-13 | 7.819-18 | 5.261-21 | 2.284-22 | | |
| SIO | 3.534 -4 | 1.064 -5 | 1.142 -7 | 2.992-10 | 8.419-14 | 5.511-19 | 1.264-28 | .000 0 | | |
| SIO2(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 3.1753-3 | 3.1815-3 | | |
| SIO2(S) | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | 3.1753-3 | .0000 0 | .0000 0 | | |
| SIO2(S) | .0000 0 | 3.1628-3 | 3.1747-3 | 3.1750-3 | 3.1751-3 | .0000 0 | .0000 0 | .0000 0 | | |
| SIO2(S) | 2.8121-3 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | .0000 0 | | |
| SIO2(L) | 1.085 -6 | 2.050 -8 | 1.221-10 | 1.461-13 | 1.388-17 | 1.810-23 | 6.277-33 | .000 0 | | |
| SIO2 | 4.106 -6 | 2.690 -7 | 1.932 -9 | 2.978-12 | 4.032-16 | 9.099-22 | 3.868-32 | .000 0 | | |
| SIS | | | | | | | | | | |

(S) = Solid

ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN .10000-05 FOR ALL ASSIGNED CONDITIONS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| AL | ALO2 | ALO2H | AL2O | AL2O2 | AL2O3(L) | C | CH | CH2 | CH2O |
| CN | CS | CS2 | C2H | CA | CAO | CASO4(S) | FE02H2(S) | FE03H3(S) | FES(S) |
| FES(S) | FES(S) | FES(L) | FESO4(S) | FES2(S) | FE2O3(S) | FE2SIO12(S) | HCN | H2SO4(L) | H2SO4 |
| K(S) | K(L) | KO | K2 | K2O(S) | K2SO4(S) | K2SO4(L) | HG(S) | HG(L) | HGH |
| HGN | HGO(L) | HGO | HGO2H2(S) | HGS(S) | HGS | MGSO4(S) | MGSO4(L) | MGTI2O5(L) | NO2 |
| N2O | NA(S) | NA(L) | NAH | NAO | NAOH(S) | NA2 | NA2O | NA2O2(S) | NA2O2(S) |
| NA2SO4(S) | NA2SO4(S) | NA2SO4(L) | NA2SO4 | O | O2 | S(S) | S(L) | SO3 | SI(S) |
| SI | SIH | TI(S) | TI(S) | TI(L) | TI | TIC(S) | TIC(L) | TIN(S) | TIN(L) |
| TIO(S) | TIO(S) | TIO(L) | TIO | TIO2(S) | TIO2(L) | TIO2 | TI2O3(S) | TI2O3(S) | TI2O3(L) |
| TI3O5(S) | TI3O5(S) | TI3O5(L) | TI4O7(S) | TI4O7(L) | | | | | |

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

## TABLE 3-3. SULFUR DISTRIBUTION, MONTANA COAL

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50% TA Temperature, $10^2$ °F | | | | | | | | 75% TA Temperature, $10^2$ °F | | | | | | | | 100% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | 3.6 | 5.9 | 2.8 | 1.3 | 1.1 | 0.6 | 0.1 | | 0.1 | 0.8 | 4.9 | 3.6 | 1.3 | 0.8 | 0.1 | | | | | | | | | |
| CaS(S) | | 8.7 | 60.8 | 80.9 | 80.9 | 80.9 | 80.9 | 48.0 | | | | 59.0 | 80.9 | 80.9 | 80.9 | 48.8 | | | | | | | 6.6 | 12.2 |
| $CaSO_4$(S) | | | | | | | | | | | | | | | | | | | | | | 45.6 | 43.6 | 36.9 |
| FeS(S) | | | | | | 6.9 | 8.1 | | | | | | | | 7.9 | | | | | | | | | |
| $H_2S$ | 36.3 | 65.0 | 34.8 | 17.7 | 18.0 | 11.6 | 8.4 | 2.6 | 0.7 | 5.0 | 37.0 | 35.1 | 17.8 | 18.3 | 8.6 | 1.8 | | | | | | 0.6 | 0.5 | 1.5 |
| $K_2SO_4$(S) | | | | | | | 2.5 | 2.5 | | | | | | | 2.5 | 2.5 | | | | | 1.9 | 2.5 | 2.5 | 2.5 |
| $Na_2SO_4$(S) | | | | | | | | 46.9 | | | | | | | | 46.9 | | | | | | 46.9 | 46.9 | 46.9 |
| $Na_2SO_4$(L) | | | | | | | | | | | | | | | | | | | | 32.0 | 46.7 | | | |
| $Na_2SO_4$ | | | | | | | | | | | | | | | | | | | 0.1 | 0.7 | | | | |
| S | 4.9 | 1.0 | | | | | | | 0.4 | 0.3 | 0.1 | | | | | | | | | | | | | |
| SH | 16.8 | 9.2 | 1.1 | 0.1 | | | | | 0.7 | 1.4 | 2.3 | 0.3 | | | | | | | | | | | | |
| SO | 18.0 | 4.1 | 0.2 | | | | | | 11.1 | 8.7 | 4.1 | 0.1 | | | | | 0.6 | 0.1 | | | | | | |
| $SO_2$ | 20.0 | 5.9 | 0.3 | | | | | | 87.0 | 87.3 | 51.7 | 2.0 | | | | | 99.4 | 99.9 | 99.9 | 67.4 | 51.4 | 4.5 | | |
| $SO_3$ | | | | | | | | | | | | | | | | | | | | | | | | |
| $S_2O$ | 0.2 | 0.1 | | | | | | | | | | | | | | | | | | | | | | |
| SiS | 0.3 | | | | | | | | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

(continued)

TABLE 3-3 (Continued).

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 125% TA Temperature, $10^2$ °F | | | | | | | | 150% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| CuS | | | | | | | | | | | | | | | | |
| CaS(S) | | | | | | | | | | | | | | | | |
| $CaSO_4$(S) | | | | 22.7 | 51.0 | 50.6 | 50.6 | 50.6 | | | | 25.5 | 51.0 | 50.6 | 50.6 | 50.6 |
| FeS(S) | | | | | | | | | | | | | | | | |
| $H_2S$ | | | | | | | | | | | | | | | | |
| $K_2SO_4$(S) | | | | | 2.2 | 2.5 | 2.5 | 2.5 | | | | | 2.2 | 2.5 | 2.5 | 2.5 |
| $Na_2SO_4$(S) | | | | | | 46.9 | 46.9 | 46.9 | | | | | | 46.9 | 46.9 | 46.9 |
| $Na_2SO_4$(L) | | | | 43.8 | 46.8 | | | | | | | 43.5 | 46.8 | | | |
| $Na_2SO_4$ | | | 1.3 | 0.8 | | | | | | | 1.4 | 1.0 | | | | |
| S | | | | | | | | | | | | | | | | |
| SH | | | | | | | | | | | | | | | | |
| SO | 0.2 | | | | | | | | | | | | | | | |
| $SO_2$ | 99.8 | 99.8 | 98.3 | 32.3 | | | | | 99.9 | 99.8 | 98.1 | 29.6 | | | | |
| $SO_3$ | 0.1 | 0.2 | 0.4 | 0.4 | | | | | 0.1 | 0.2 | 0.5 | 0.4 | | | | |
| $S_2O$ | | | | | | | | | | | | | | | | |
| SiS | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

## TABLE 3-4. SULFUR DISTRIBUTION, LIGNITE

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50% TA Temperature, $10^2$ °F | | | | | | | | 75% TA Temperature, $10^2$ °F | | | | | | | | 100% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | 4.0 | 6.6 | 3.1 | 1.2 | 0.3 | | | | 0.1 | 0.7 | 5.2 | 3.7 | 0.8 | 0.1 | | | | | | | | | 12.0 | 17.2 |
| CaS(S) | | 20.9 | 68.5 | 87.5 | 96.4 | 99.4 | 96.6 | 89.9 | | | | 88.2 | 90.6 | 98.2 | 96.6 | 90.3 | | | | | 8.7 | 85.3 | 79.0 | 73.4 |
| $CaSO_4$(S) | | | | | | | | | | | | | | | | | | | | | | 1.0 | 0.3 | 0.8 |
| $H_2S$ | 28.0 | 50.6 | 26.8 | 11.3 | 3.3 | 0.5 | 0.2 | 1.5 | 0.4 | 3.2 | 27.9 | 25.7 | 8.6 | 1.7 | 0.2 | 1.0 | | | | | 3.0 | 3.2 | 3.2 | 3.2 |
| $K_2SO_4$(S) | | | | | | | 3.2 | 3.2 | | | | | | | 3.2 | 3.2 | | | | | | 5.4 | 5.4 | 5.4 |
| $Na_2SO_4$(S) | | | | | | | | 5.4 | | | | | | | | 5.4 | | | | 0.3 | 5.3 | | | |
| $Na_2SO_4$(L) | | | | | | | | | | | | | | | | | | | | 0.6 | | | | |
| $Na_2SO_4$ | | | | | | | | | | | | | | | | | | | | | | | | |
| S | 5.0 | 1.1 | | | | | | | 0.4 | 0.3 | 0.1 | | | | | | | | | | | | | |
| SH | 14.9 | 8.2 | 1.0 | 0.1 | | | | | 0.5 | 1.1 | 2.0 | 0.2 | | | | | | | | | | | | |
| SO | 21.0 | 4.8 | 0.2 | | | | | | 10.1 | 8.2 | 4.4 | 0.1 | | | | | 0.6 | 0.1 | | | | | | |
| $SO_2$ | 26.8 | 7.8 | 0.4 | | | | | | 88.5 | 86.6 | 60.3 | 2.1 | | | | | 99.5 | 99.9 | 100.0 | 99.1 | 83.0 | 5.0 | | |
| $SO_3$ | | | | | | | | | | | 0.2 | | | | | | | | | | | | | |
| $S_2O$ | 0.2 | | | | | | | | | | | | | | | | | | | | | | | |
| SiS | 0.3 | | | | | | | | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

Reproduced from best available copy.

(Continued)

TABLE 3-4 (Continued).

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 125% TA Temperature, $10^2$ °F | | | | | | | | 150% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | | | | | | | | | | | | | | | | |
| CaS(S) | | | | | | | | | | | | | | | | |
| $CaSO_4$(S) | | | | 67.1 | 91.7 | 91.4 | 91.4 | 91.4 | | | | 69.6 | 91.7 | 91.4 | 91.4 | 91.4 |
| $H_2S$ | | | | | | | | | | | | | | | | |
| $F_2SO_4$(S) | | | | | 3.0 | 3.2 | 3.2 | 3.2 | | | | | 3.0 | 3.2 | 3.2 | 3.2 |
| $Na_2SO_4$(S) | | | | | | 5.4 | 5.4 | 5.4 | | | | | | 5.4 | 5.4 | 5.4 |
| $Na_2SO_4$(L) | | | | 2.9 | 5.3 | | | | | | | 2.6 | 5.3 | | | |
| $Na_2SO_4$ | | | | 0.8 | | | | | | | | 0.9 | | | | |
| S | | | | | | | | | | | | | | | | |
| SH | | | | | | | | | | | | | | | | |
| SO | 0.2 | | | | | | | | | | | | | | | |
| $SO_2$ | 99.8 | 99.8 | 99.6 | 29.0 | | | | | 99.9 | 99.8 | 99.5 | 26.6 | | | | |
| $SO_3$ | 0.1 | 0.2 | 0.4 | 0.3 | | | | | 0.1 | 0.2 | 0.5 | 0.4 | | | | |
| $S_2O$ | | | | | | | | | | | | | | | | |
| SiS | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

## TABLE 3-5. SULFUR DISTRIBUTION, AUGMENTED LIGNITE

| | Weight % of Total Sulfur | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50% TA Temperature, $10^2$ °F | | | | | | | | 75% TA Temperature, $10^2$ °F | | | | | | | | 100% TA Temperature, $10^2$ °F | | | | | | | |
| Species | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | 3.3 | 6.9 | 3.3 | 1.2 | 0.3 | | | | 0.1 | 0.7 | 4.7 | 1.4 | 0.8 | 0.1 | | | | | | | | 0.1 | | |
| CaS(S) | | 6.1 | 63.4 | 85.3 | 95.7 | 99.3 | 98.1 | 100.0 | | | | 66.5 | 89.9 | 98.1 | 98.1 | 92.6 | | | | | | 17.4 | 37.7 | 42.8 |
| $CaSO_4$(S) | | | | | | | | | | | | | | | | | | | | | | 66.9 | 55.7 | 50.0 |
| $H_2S$ | 25.8 | 58.7 | 31.4 | 13.4 | 4.1 | 0.7 | 0.2 | | 0.5 | 3.4 | 28.8 | 27.5 | 9.3 | 1.8 | 0.2 | 1.2 | | | | | 0.1 | 3.3 | 0.4 | 1.0 |
| $K_2SO_4$(S) | | | | | | | 1.7 | | | | | | | | 1.7 | 1.8 | | | | | 1.2 | 1.8 | 1.8 | 1.8 |
| $Na_2SO_4$(S) | | | | | | | | | | | | | | | | 4.5 | | | | | | 4.5 | 4.5 | 4.5 |
| $Na_2SO_4$(L) | | | | | | | | | | | | | | | | | | | | | 4.3 | | | |
| $Na_2SO_4$ | | | | | | | | | | | | | | | | | | | | | | | | |
| S | 4.3 | 1.1 | | | | | | | 0.3 | 0.3 | 0.1 | | | | | | | | | | | | | |
| SH | 13.3 | 9.3 | 1.1 | 0.1 | | | | | 0.5 | 1.1 | 1.9 | 0.2 | | | | | | | | | | | | |
| SO | 21.3 | 6.1 | 0.2 | | | | | | 9.9 | 7.9 | 4.2 | 0.1 | | | | | 0.6 | 0.2 | 0.1 | | | | | |
| $SO_2$ | 31.7 | 11.7 | 0.6 | | | | | | 88.7 | 86.7 | 60.0 | 2.2 | | | | | 99.4 | 99.9 | 99.9 | 100.0 | 94.5 | 6.1 | | |
| $SO_3$ | | | | | | | | | | | | | | | | | | | | | | | | |
| $S_2O$ | 0.2 | 0.2 | | | | | | | | | 0.2 | | | | | | | | | | | | | |
| SiS | 0.2 | | | | | | | | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

(Continued)

TABLE 3-5 (Continued).

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 125% TA Temperature, $10^2$ °F | | | | | | | | 150% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | | | | | | | | | | | | | | | | |
| CaS(S) | | | | | | | | | | | | | | | | |
| $CaSO_4$(S) | | | | 69.9 | 94.0 | 93.8 | 93.8 | 93.8 | | | | 72.4 | 94.1 | 93.8 | 93.8 | 93.8 |
| $K_2S$ | | | | | | | | | | | | | | | | |
| $K_2SO_4$(S) | | | | | 1.5 | 1.8 | 1.8 | 1.8 | | | | | 1.5 | 1.8 | 1.8 | 1.8 |
| $Na_2SO_4$(S) | | | | | | 4.5 | 4.5 | 4.5 | | | | | | 4.5 | 4.5 | 4.5 |
| $Na_2SO_4$(L) | | | | 2.0 | 4.4 | | | | | | | 1.7 | 4.4 | | | |
| $Na_2SO_4$ | | | | 0.7 | | | | | | | | 0.8 | | | | |
| S | | | | | | | | | | | | | | | | |
| SH | | | | | | | | | | | | | | | | |
| SO | 0.2 | | | | | | | | | | | | | | | |
| $SO_2$ | 99.8 | 99.8 | 99.6 | 27.0 | | | | | 99.9 | 99.8 | 99.5 | 24.7 | | | | |
| $SO_3$ | 0.1 | 0.2 | 0.4 | 0.3 | | | | | 0.1 | 0.2 | 0.5 | 0.4 | | | | |
| $S_2O$ | | | | | | | | | | | | | | | | |
| SiS | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

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## TABLE 3-6. SULFUR DISTRIBUTION, PITTSBURGH #8

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 50% TA Temperature, $10^2$ °F | | | | | | | | 75% TA Temperature, $10^2$ °F | | | | | | | | 100% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| CuS | 4.7 | 8.0 | 7.2 | 5.7 | 5.0 | 4.5 | 0.7 | | 0.2 | 0.9 | 5.8 | 11.0 | 5.7 | 3.7 | 1.1 | | | | | | | | | |
| CaS(S) | | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | | | | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | | | | | | | | |
| $CaSO_4$(S) | | | | | | | | | | | | | | | | | | | | | 4.7 | 4.7 | 4.7 | 4.7 |
| FeS(S) | | | | 31.9 | 32.0 | 32.0 | 32.0 | | | | | | 31.9 | 31.9 | 31.9 | | | | | | | | | |
| FeS(L) | | | 19.7 | | | | | | | | | | | | | | | | | | | | | |
| $FeS_2$(S) | | | | | | | | 63.9 | | | | | | | | 63.9 | | | | | | | | 4.6 |
| $Fe_2(SO_4)_3$(S) | | | | | | | | | | | | | | | | | | | | | | | | |
| $H_2S$ | 35.5 | 65.9 | 65.2 | 57.4 | 58.3 | 58.9 | 59.8 | 28.6 | 0.6 | 4.0 | 31.7 | 77.8 | 57.6 | 59.6 | 59.4 | 28.6 | | | | | | | 1.6 | 0.2 |
| $H_2SO_4$ | | | | | | | | | | | | | | | | | | | | | | | | |
| $K_2SO_4$(S) | | | | | | | 2.2 | 2.2 | | | | | | | 2.2 | 2.2 | | | | | 2.1 | 2.2 | 2.2 | 2.2 |
| $K_2SO_4$(L) | | | | | | | | | | | | | | | | | | | | | | | | |
| $MgSO_4$(S) | | | | | | | | | | | | | | | | | | | | | | | | 2.1 |
| $Na_2SO_4$(S) | | | | | | | 0.7 | 0.7 | | | | | | | 0.7 | 0.7 | | | | | | 0.7 | 0.7 | 0.7 |
| $Na_2SO_4$(L) | | | | | | | | | | | | | | | | | | | | | 0.6 | | | |
| $Na_2SO_4$ | | | | | | | | | | | | | | | | | | | | | | | | |
| S | 5.9 | 1.3 | 0.1 | | | | | | 0.4 | 0.3 | 0.2 | | | | | | | | | | | | | |
| SO | 18.2 | 10.4 | 2.3 | 0.3 | | | | | 0.6 | 1.3 | 2.2 | 0.7 | | | | | | | | | | | | |
| SO | 18.3 | 4.3 | 0.3 | | | | | | 11.1 | 8.8 | 4.4 | 0.3 | | | | | 0.6 | 0.1 | | | | | | |
| $SO_2$ | 17.3 | 5.3 | 0.5 | | | | | | 87.2 | 84.6 | 55.4 | 5.4 | | | | | 99.5 | 99.9 | 100.0 | 100.0 | 92.6 | 92.5 | 90.9 | 85.6 |
| $SO_3$ | | | | | | | | | | | | | | | | | | | | | | | | |
| $S_2O$ | 0.3 | 0.2 | | | | | | | | 0.1 | 0.3 | 0.1 | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(s) = solid

(Continued)

TABLE 3-6 (Continued).

| Species | Weight % of Total Sulfur | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 125% TA Temperature, $10^2$ °F | | | | | | | | 150% TA Temperature, $10^2$ °F | | | | | | | |
| | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 | 33 | 29 | 25 | 21 | 17 | 13 | 9 | 5 |
| COS | | | | | | | | | | | | | | | | |
| CaS(S) | | | | | | | | | | | | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 |
| $CaSO_4$(S) | | | | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | | | | | | | | |
| FeS(S) | | | | | | | | | | | | | | | | |
| FeS(L) | | | | | | | | | | | | | | | | |
| $FeS_2$(S) | | | | | | | | | | | | | | | 47.9 | 47.9 |
| $Fe_2(SO_4)_3$(S) | | | | | | | 47.9 | 47.9 | | | | | | | | |
| $H_2S$ | | | | | | | | | | | | | | | 0.3 | 35.8 |
| $H_2SO_4$ | | | | | | | 0.3 | 36.7 | | | | | | | | |
| $K_2SO_4$(S) | | | | | 2.2 | 2.2 | 2.2 | 2.2 | | | | | 2.2 | 2.2 | 2.2 | 2.2 |
| $K_2SO_4$(L) | | | | 0.9 | | | | | | | | 0.8 | | | | |
| $MgSO_4$(S) | | | | | | 2.1 | 2.1 | 2.1 | | | | | | 2.1 | 2.1 | 2.1 |
| $Na_2SO_4$(S) | | | | | | 0.7 | 0.7 | 0.7 | | | | | | 0.7 | 0.7 | 0.7 |
| $Na_2SO_4$(L) | | | | | 0.7 | | | | | | | | 0.7 | | | |
| $Na_2SO_4$ | | | | 0.3 | | | | | | | | 0.3 | | | | |
| S | | | | | | | | | | | | | | | | |
| SH | | | | | | | | | 0.1 | | | | | | | |
| SO | 0.2 | | | | | | | | | | | | | | | |
| $SO_2$ | 99.8 | 99.8 | 99.6 | 93.1 | 87.9 | 61.3 | 2.4 | | 99.8 | 99.8 | 99.5 | 92.8 | 86.7 | 55.9 | 1.9 | |
| $SO_3$ | 0.1 | 0.2 | 0.4 | 1.1 | 4.6 | 29.1 | 39.8 | 5.8 | 0.1 | 0.2 | 0.5 | 1.4 | 5.8 | 34.5 | 40.3 | 6.7 |
| $S_2O$ | | | | | | | | | | | | | | | | |

Note: Only non-zero entries are shown.

(S) = solid

TABLE 3-7. SULFUR RETENTION BY CONDENSED SPECIES

Weight % of Total Sulfur

| Coal | % TA | Temperature, °F 3300 | 2900 | 2500 | 2100 | 1700 | 1300 | 900 | 500 |
|---|---|---|---|---|---|---|---|---|---|
| Montana | 50 | 0 | 8.7 | 60.8 | 80.9 | 80.9 | 87.8 | 91.5 | 97.4 |
| | 75 | 0 | 0 | 0 | 59.0 | 80.9 | 80.9 | 91.2 | 98.2 |
| | 100 | 0 | 0 | 0 | 32.0 | 48.6 | 95.0 | 99.5 | 98.6 |
| | 125 | 0 | 0 | 0 | 66.5 | 100.0 | 100.0 | 100.0 | 100.0 |
| | 150 | 0 | 0 | 0 | 68.9 | 100.0 | 100.0 | 100.0 | 100.0 |
| Lignite | 50 | 0 | 20.9 | 68.5 | 87.5 | 96.4 | 99.4 | 99.8 | 98.5 |
| | 75 | 0 | 0 | 0 | 68.2 | 90.6 | 98.2 | 99.8 | 99.0 |
| | 100 | 0 | 0 | 0 | 0.3 | 17.0 | 94.0 | 99.7 | 99.2 |
| | 125 | 0 | 0 | 0 | 69.9 | 100.0 | 100.0 | 100.0 | 100.0 |
| | 150 | 0 | 0 | 0 | 72.1 | 100.0 | 100.0 | 100.0 | 100.0 |
| Augmented Lignite | 50 | 0 | 6.1 | 63.4 | 85.3 | 95.7 | 99.3 | 99.8 | 100.0 |
| | 75 | 0 | 0 | 0 | 66.5 | 89.9 | 98.1 | 99.8 | 98.8 |
| | 100 | 0 | 0 | 0 | 0 | 5.5 | 90.5 | 99.7 | 99.1 |
| | 125 | 0 | 0 | 0 | 72.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | 150 | 0 | 0 | 0 | 74.2 | 100.0 | 100.0 | 100.0 | 100.0 |
| Pittsburgh #8 | 50 | 0 | 4.7 | 24.3 | 36.6 | 36.6 | 36.6 | 39.5 | 71.4 |
| | 75 | 0 | 0 | 0 | 4.7 | 36.6 | 36.6 | 39.5 | 71.4 |
| | 100 | 0 | 0 | 0 | 0 | 7.4 | 7.5 | 7.5 | 14.2 |
| | 125 | 0 | 0 | 0 | 5.6 | 7.5 | 9.6 | 57.5 | 57.5 |
| | 150 | 0 | 0 | 0 | 5.5 | 7.5 | 9.6 | 57.5 | 57.5 |

As previously mentioned, Pittsburgh #8 had a low calcium content in comparison with the other coals--by at least a factor of 10. An examination was made of the computer output at 500 °F for all coals in order to perform calcium, potassium and sodium mass balances with the results shown in Table 3-8. The results were that all the calcium in Pittsburgh #8 combined with sulfur to form CaS(s) at 50 and 75% theoretical air, and form $CaSO_4$(s) at the higher air levels. The calcium in the other three coals was present in sufficient quantities so that it formed $Ca(OH)_2$(s), a non-sulfur containing compound, in addition to CaS(s) and $CaSO_4$(s). The additional calcium (as CaO) in augmented lignite appears to be converted directly to additional $Ca(OH)_2$(s), instead of forming additional condensed sulfur compounds.

Aside from augmented lignite at 50% theoretical air, all the potassium and sodium was associated with their respective sulfates.

Based on the results of thermochemical equilibrium considerations, it may be possible to increase the condensed phase sulfur retention of Pittsburgh #8 coal by augmentation primarily with calcium (as CaO). Augmentation with potassium and/or sodium does not appear to offer significantly greater condensed phase sulfur retention.

## 3.5 DISCUSSION OF THE EQUILIBRIUM RESULTS

The potential performance of sulfur retention by the ash for different combustion modes can be demonstrated by observing the predicted equilibrium ash composition at the various theoretical air levels and temperatures for the Montana coal shown in Table 3-3. The combustion modes considered are:

- pulverized coal combustion
- fuel bed coal combustion
- cyclone coal combustor

The degree of sulfur retention in each of these combustion systems is governed by the equilibrium consideration of:

- ash composition
- temperature
- stoichiometry

TABLE 3-8. MASS BALANCES FOR CALCIUM, POTASSIUM AND SODIUM AT 500 °F

Weight Percent of Total Element

| Coal | Element | Percent Theoretical Air (by Weight) 50 | 75 | 100 | 125 | 150 |
|---|---|---|---|---|---|---|
| Montana | Calcium | 40.6% $Ca(OH)_2$ (S), 59.4% CaS (S) | 39.7% $Ca(OH)_2$ (S), 60.3% CaS (S) | 39.2% $Ca(OH)_2$ (S), 15.1% CaS (S), 45.7% $CaSO_4$ (S) | 37.4% $Ca(OH)_2$ (S), 62.6% $CaSO_4$ (S) | 37.4% $Ca(OH)_2$ (S), 62.6% $CaSO_4$ (S) |
| | Potassium | 100% $K_2SO_4$ (S) → | | | | |
| | Sodium | 100% $Na_2SO_4$ (S) → | | | | |
| Lignite | Calcium | 32.0% $Ca(OH)_2$ (S), 68.3% CaS (S) | 31.7% $Ca(OH)_2$ (S), 68.3% CaS (S) | 31.5% $Ca(OH)_2$ (S), 13.0% CaS (S), 55.5% $CaSO_4$ (S) | 30.9% $Ca(OH)_2$ (S), 69.1% $CaSO_4$ (S) | 30.9% $Ca(OH)_2$ (S), 69.1% $CaSO_4$ (S) |
| | Potassium | 100% $K_2SO_4$ (S) → | | | | |
| | Sodium | 100% $Na_2SO_4$ (S) → | | | | |
| Augmented Lignite | Calcium | 100% CaS (S) | 75.6% $Ca(OH)_2$ (S), 24.4% CaS (S) | 75.5% $Ca(OH)_2$ (S), 11.3% CaS (S), 13.2% $CaSO_4$ (S) | 75.3% $Ca(OH)_2$ (S), 24.7% $CaSO_4$ (S) | 75.3% $Ca(OH)_2$ (S), 24.7% $CaSO_4$ (S) |
| | Potassium | 100% $K_2(OH)_2$ | 100% $K_2SO_4$ (S) → | | | |
| | Sodium | 100% NaOH (S) | 100% $Na_2SO_4$ (S) → | | | |
| Pittsburgh #8 | Calcium | 100% CaS (S) | 100% CaS (S) | 100% $CaSO_4$ (S) → | | |
| | Potassium | 100% $K_2SO_4$ (S) → | | | | |
| | Sodium | 100% $Na_2SO_4$ (S) → | | | | |

On top of these considerations must be added

- mixing or contact of sulfur with metals
- kinetic limitations of the sulfur reactions
- temperature and stoichiometry as a function of time in the combustor

Each of these factors will be discussed for each combustor type listed above.

The equilibrium calculation show that calcium and sodium are the major species that combine with sulfur and form liquids or solids at temperatures in the furnace.

### 3.5.1 Pulverized Coal

In a pulverized coal flame the reactants are fairly well mixed so that good contact of the sulfur and metals should occur. However when the coal particles approach the flame they are heated and begin to devolatilize the carbon, hydrogen, and sulfur. The metals in the ash are concentrated in the particle until such time as they are heated to their melting point or vaporize. In a pulverized coal flame it is very difficult to make the gas phase fuel rich. The overall bulk stoichiometry may be fuel rich but in the flame the rate of devolatilization and combustion is not sufficiently rapid to make the gaseous region surrounding the coal particle fuel rich. Therefore there is always oxygen available to form sulfur oxides. This along with the equilibrium constraints are the reasons that large amounts of $SO_2$ are formed even in sub-stoichiometric flames.

The temperature and stoichiometry history of the coal particle can severely affect the sulfur retention. For example, as the particle heats up it passes through a low temperature fuel rich region where the predicted equilibrium products are calcium sulfide. However, if these products are formed in this stage they ultimately pass into a high temperature oxidizing region where the favored equilibrium products are $SO_2$. Controlling the temperature of this stage of the flame can shift the favored equilibrium products to $CaSO_4$ and $Na_2SO_4$.

It is interesting to note that the same control measures that favor low $NO_x$ emissions from P.C. coal flames are also the condition that should favor high sulfur retention by the metals in the coal ash. These conditions

are staged combustion with a fuel rich first stage followed by excess air addition to render the mixture oxidizing. However this excess air addition stage is critical in terms of both $NO_x$ and sulfur retention. $NO_x$ emissions are a strong function of excess air in the second stage. The goal in terms of $NO_x$ is to supply just enough second stage air to complete carbon burn out. This will be the minimum acceptable $NO_x$ point. In the case of sulfur retention, increasing the excess air in the second stage favors the condensed sulfate below 2500 °F. Table 3-3 shows that a minimum in the condensed phase sulfur species occurs at the stoichiometric point, TA = 100, at the optimum retention temperature, below 2500 °F. Condensed phase sulfides are formed at low stoichiometric ratios, this shifts to the sulfates at high stoichiometric ratios. Therefore the conditions for high sulfur retention predicted from thermodynamic equilibrium are temperatures below 2500 °F and theoretical air of 125%.

The reactivity of sodium compounds such as sodium bicarbonate with $SO_2$ is well known and forms the foundation for the dry $SO_2$ adsorption processes using nahcolite (mostly $NaHCO_3$) and trona (mostly $Na_2CO_3$).

The reaction of sodium with $SO_2$ is thought to proceed via an adsorption step followed by reaction to form the sulfate. This has been demonstrated in baghouses by Shah, et al. (Ref. 3) in which a filter cake containing nahcolite continued to remove $SO_2$ from the flue gas stream after the sorbent injection had been stopped. The reactions also occur in suspension presumably by adsorption onto the sorbent particles.

The reaction of calcium with $SO_2$ is also thought to be a heterogeneous process. Therefore the contact and mixing processes at the lower temperatures is important. In pulverized coal flames 80 to 90 percent of the ash is still suspended in the flue gas in the convective section where the temperatures for good sulfur capture occur. For the case where sufficient sodium is present in the ash the only parameter limiting the attainment of the full thermodynamic equilibrium product would be kinetic considerations. Such kinetic limitations might be:

- insufficient surface area
- inactive surface

It is well established that sodium can capture sulfur via a heterogeneous reaction with $SO_2$. However the reaction of calcium with sulfur under reducing conditions can form the sulfide. This reaction is more than likely heterogeneous, as well as the reaction steps that take the calcium sulfide to calcium sulfate. Calcium therefore has a fuel rich reaction mode that the sodium doesn't have. This mode may be important under the strongly reducing condition exhibited by such combustion systems as the fuel bed and the cyclone burner.

### 3.5.2 Fuel Bed Coal Combustion

Combustion systems that operate with the bulk of the combustion taking place in a thick bed of coal have characteristically low flue gas particulate loadings. Most of the ash is retained on the bed and discharged into the ash pit. Combustion takes place within much larger coal particles and as such, a larger component of the burning is of a diffusion nature. The bulk temperature of the fuel bed increases from the grate where the combustion air is supplied to the top of the bed which receives radiant heat from furnace as well as from exothermic reactions. However, within the fuel bed surrounding individual coal particles, the temperature is not well defined. The coal particle itself will have a temperature gradient from the coal core to a hot surface. As the particle heats up, the coal devolatilizes and thermally cracks. The ash inclusions within the particle can conceivably experience a temperature stoichiometry history that is conducive to sulfur retention. Within these inclusions, the calcium could react with sulfur to form the sulfide under the fuel rich condition. Due to the nature of the combustion, and the cooling effect of the combustion air, these ash packets may never experience a temperature emission high enough to decompose the calcium sulfide compound to $SO_2$.

The stoichiometry in the fuel bed varies through the bed and around the coal particles. The sulfur retention will be lessened to the extent that the variation from the optimum conditions are great.

The fact that sulfur is retained in a fuel bed system, coupled with the dependence on calcium content of the coal, point to a rather different reaction mechanism than is found with sodium sulfur capture. The specific surface area of the coal/ash mixture in the fuel bed is many times less than the surface area of the fly ash particles from a pulverized coal flame. This combined with the condition that most of the ash remains in the bed and is not in intimate contact with the $SO_2$ in the flue gas indicates that the sulfur migrates through the bed until contact with the metals occurs.

In a well controlled laboratory fuel bed simulator, sulfur balances have been made on the gaseous $SO_2$ emissions and the sulfur retained in the ash. Table 3-9 contains the data for the solids analysis and gas analysis. Under the solids analysis three layers of the fuel bed were analyzed separately; the top unburned coal, the middle partially burned coal, and the ash layer. The ash was used as a tracer and the pounds of sulfur per pounds of ash are shown for each layer. Based on the top coal layer and the ash layer, the ash retained 57% of the available sulfur. Also shown in this table are the gaseous measurements of $SO_2$ emitted during the test burn. The theoretical maximum $SO_2$ emission at 3% excess $O_2$ is 783 ppm. The measured value of 364 ppm represents a 54% retention. This compares very well with the solids analysis. This test was performed on a coal that had been ground, mixed with additional lime and reformed into briquettes. The lime addition brought the Ca/S molar ratio up to 1.65 from the naturally occuring ratio of 0.60 in the coal. This information implies that only 35% of the available calcium in the fuel bed was effective in retaining sulfur.

### 3.5.3 Cyclone Coal Combustor

No test data are available on sulfur retention in cyclone furnaces. However these systems represent what might be optimal conditions for large retentions. The cyclone is a relatively well mixed system in which most of the ash remains in the combustor. This mixing provides good contact of metals and sulfur. The slag layer temperatures are in the range of 2000 to 2500 °F since this represents the range of fluid temperatures of most coal ashes under reducing conditions. The slag layer collects the larger raw incoming coal particles which devolatilize and burn in the slag. Smaller particles remain

TABLE 3-9. SULFUR BALANCES ON A LABORATORY FUEL BED SIMULATOR

| Solids Analysis | Top Coal - 8-9" | Middle Coal 20.5-21.5" | Ash |
|---|---|---|---|
| Moisture, % | 41.89 | 2.12 | 0.12 |
| Ash, % | 8.45 | 18.78 | 96.68* Dry Basis |
| Sulfur, % | 0.47 | 0.74 | 3.06* |
| Gross Heat of Combustion | 9796* | 10,200* | -- |
| Net Heat of Combustion | 9366* | 9923* | -- |
| lb Sulfur/lb Ash | 0.0556 | 0.0394 | 0.0317 (57% retention) |

Ca/S (molar) = 1.65

| Gaseous Analysis | $SO_2$ at 3% $O_2$, ppm |
|---|---|
| Theo. max. | 783 |
| Measured | 364 |
| Percent retention | 54 |

entrained in the gas stream where they burn. Exit gas temperatures from the cyclone are higher than 2500 °F, however the molten slag layer loses heat to the water-cooled furnace walls and typically remains just hot enough to flow out of the furnace. The conditions of rapid mixing, temperatures below 2500 °F, and containment of most of the ash would presumably favor a high degree of sulfur retention. The equilibrium calculation predict significant quantities of liquid sodium sulfate at 2100 °F at 125% theoretical air. The addition of sodium fluxing compounds to a coal ash usually lowers the fluid temperature of the slag. Such action would be in the right direction for increased sulfur retention by both calcium and sodium.

Although it has not been the practice in the past, cyclone combustors could be run at substoichiometric fuel to air ratios with secondary air addition to complete burnout. Such a system would be similar to the two stage low $NO_x$ combustor developed at B&W (Ref. 4). However by running the cyclone first stage fuel rich the ash fluid temperatures could be reduced to the 2000 °F region. Under reducing conditions at these temperatures calcium sulfide is a favored product which would be removed with the slag.

It would be desirable in order to control sulfur oxides emissions to investigate the sulfur retention characteristics of cyclone combustors and to change the process variables in order to optimize the retention of sulfur in the slag.

# SECTION 4.0

# CONCLUSIONS

The results of field tests, laboratory tests and equilibrium calculations show that sulfur can be retained in coal ash by reacting with the calcium, sodium and potassium components of that ash under reducing as well as oxidizing conditions. Sodium sulfate is the only condensed phase sulfur compound that occurs as a liquid.

The field data generally indicated that increasing boiler load and excess $O_2$ results in increased sulfur retention. This conclusion is supported by the equilibrium calculation which showed increasing retention with increasing excess $O_2$ up to temperatures of 2100 °F. At this temperature a minimum sulfur retention was exhibited as the fuel/air mixture passed through the stoichiometric condition. The retention then increased as the mixture became increasingly fuel rich.

Although the results do not indicate the mechanism for the sulfur retention they do point to the condition under which the retention could be expected. The three major modes of coal combustion, pulverized, fuel bed and cyclone combustion were analyzed in terms of the potential for sulfur retention in each. The assessment concluded that the new developing low $NO_x$ technology for coal combustion also produces the conditions of stoichiometry and temperature that are necessary for enhanced sulfur retention.

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